Supporting Information

Exploring the Application of the Negishi Reaction of HaloBODIPYs: Generality, Regioselectivity and Synthetic Utility in the Development of BODIPY Laser Dyes

Eduardo Palao,[†] Gonzalo Duran-Sampedro,[†] Santiago de la Moya,*[,†] Miriam Madrid,[†] Carmen García-López, [†] Antonia R. Agarrabeitia,[†] Bram Verbelen,[‡] Wim Dehaen, [‡] Nöel Boens[‡] and María J. Ortiz*[,†]

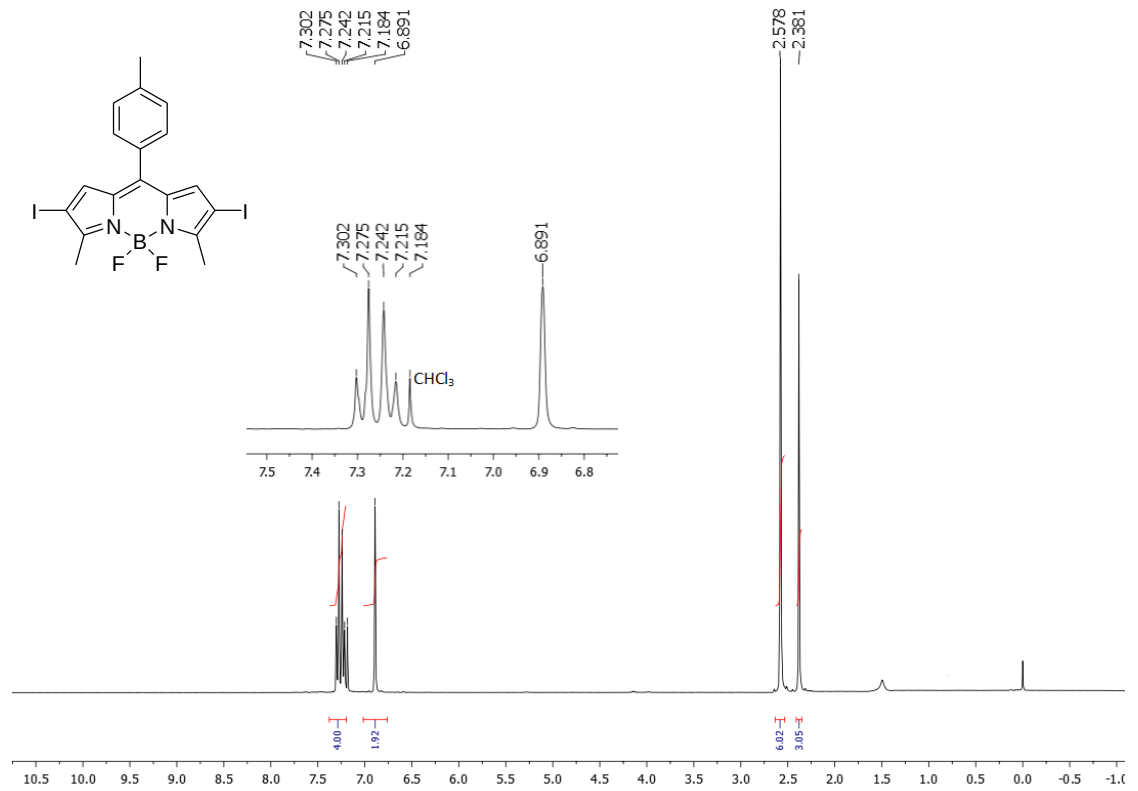
[†]Department of Organic Chemistry I, Universidad Complutense de Madrid, Facultad de Ciencias Químicas, Ciudad Universitaria s/n, E-28040 Madrid, Spain

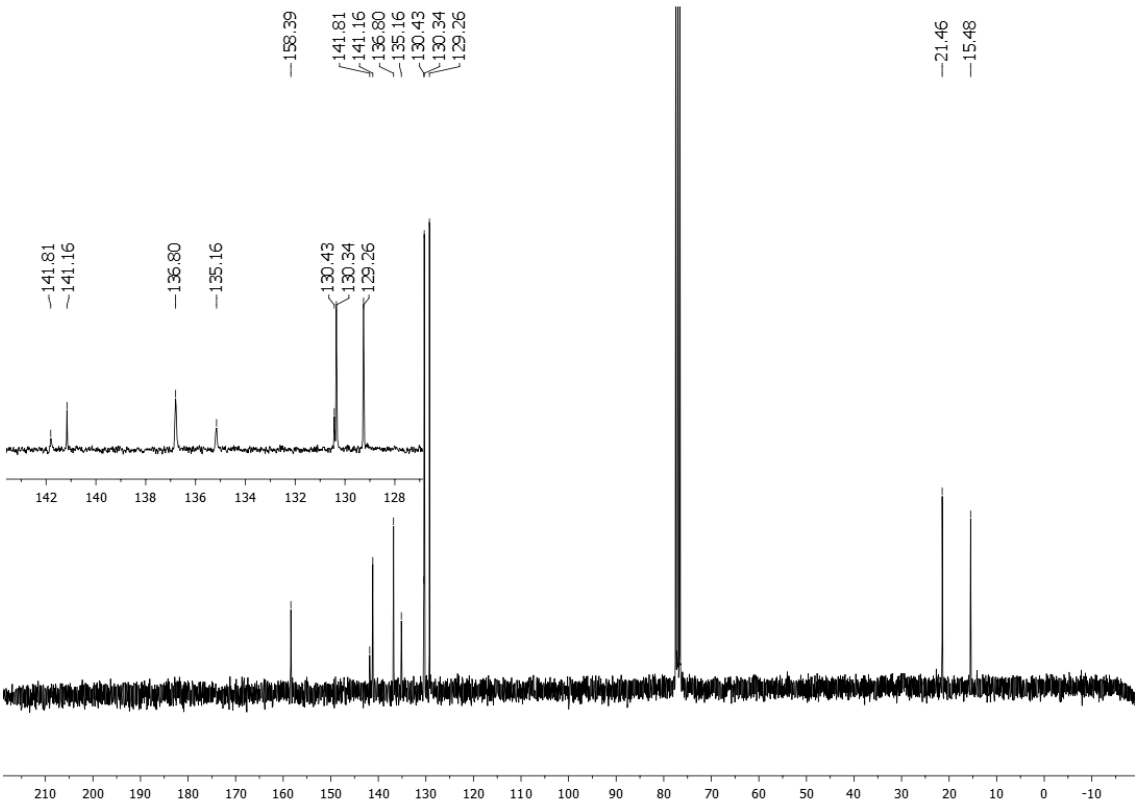
[‡]Department of Chemistry, KU Leuven, Celestijnenlaan 200 f, B-3001 Leuven, Belgium

Table of Contents

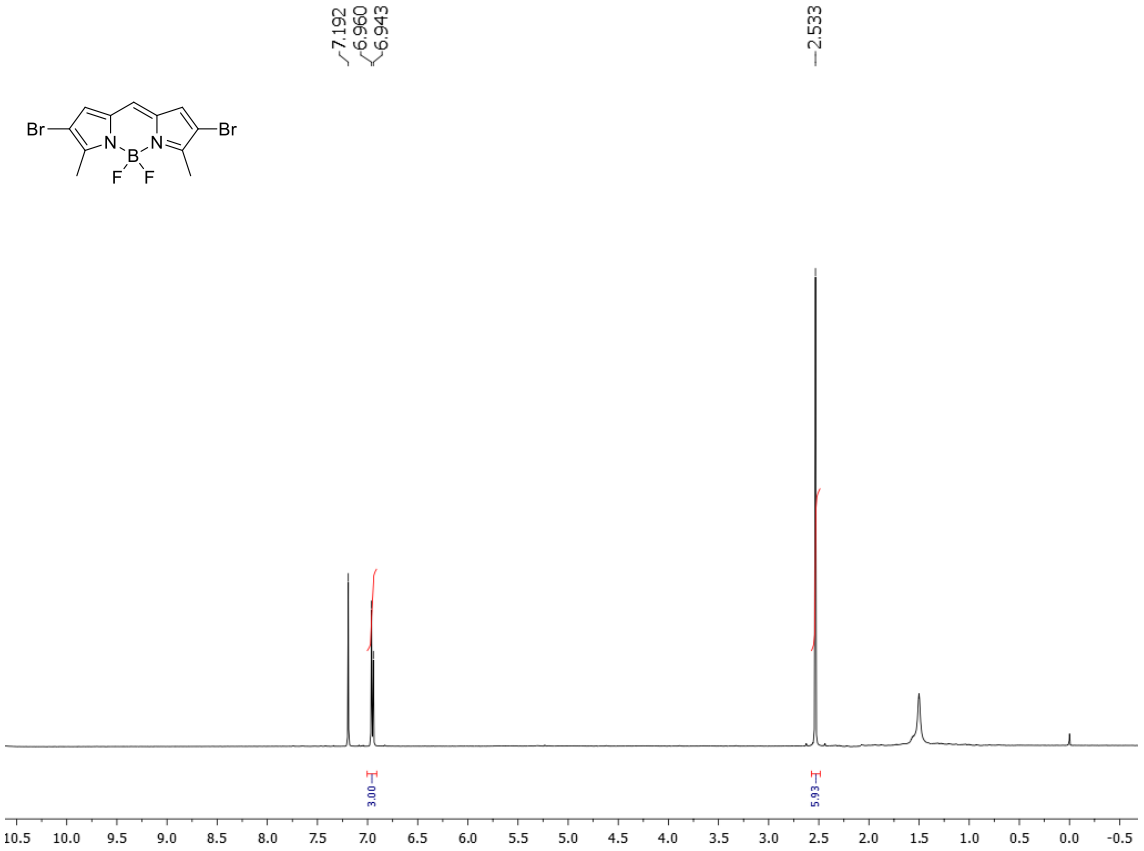
1. ^{1}H NMR and ^{13}C NMR Spectra

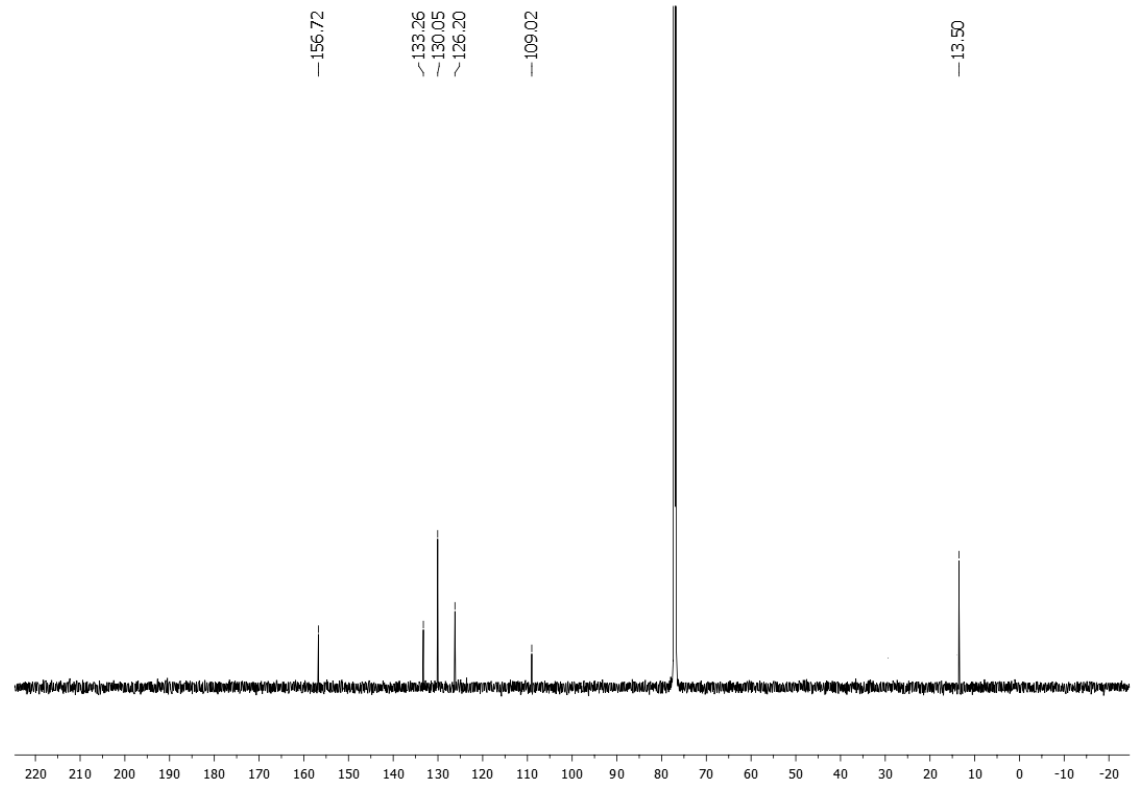
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of **3d**



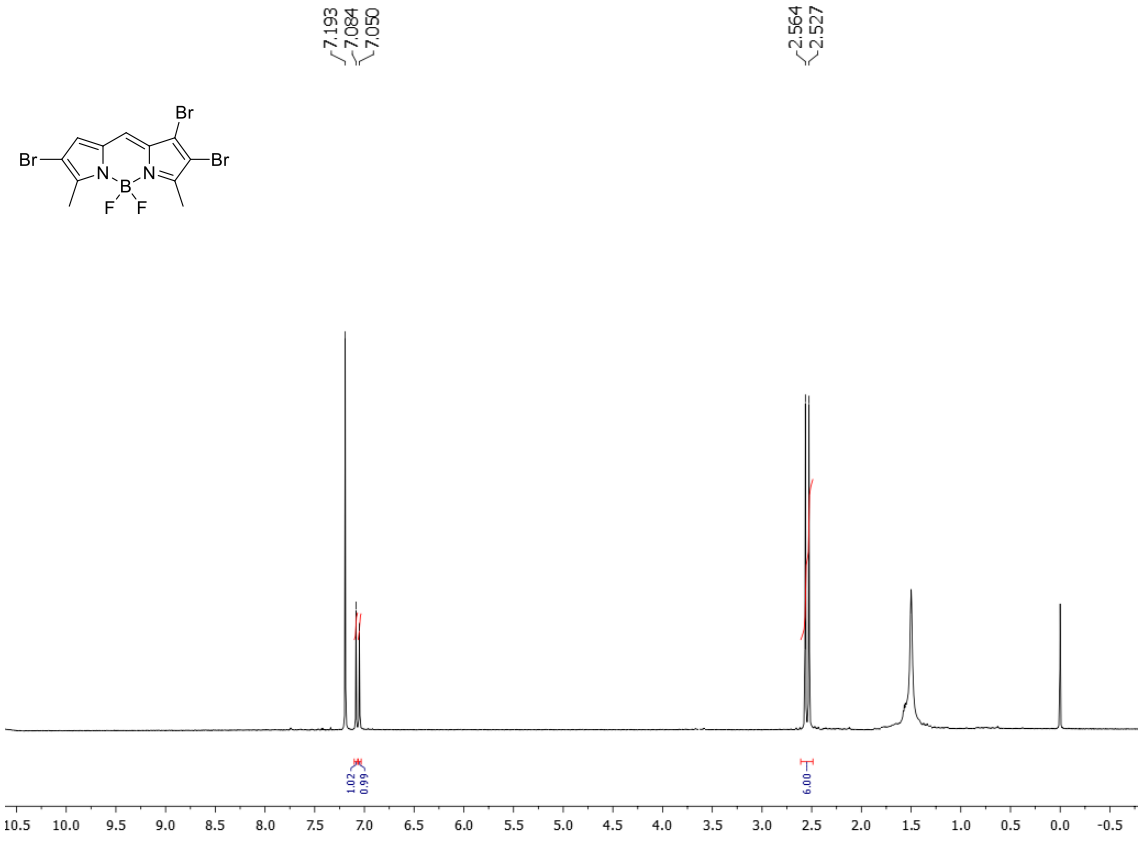


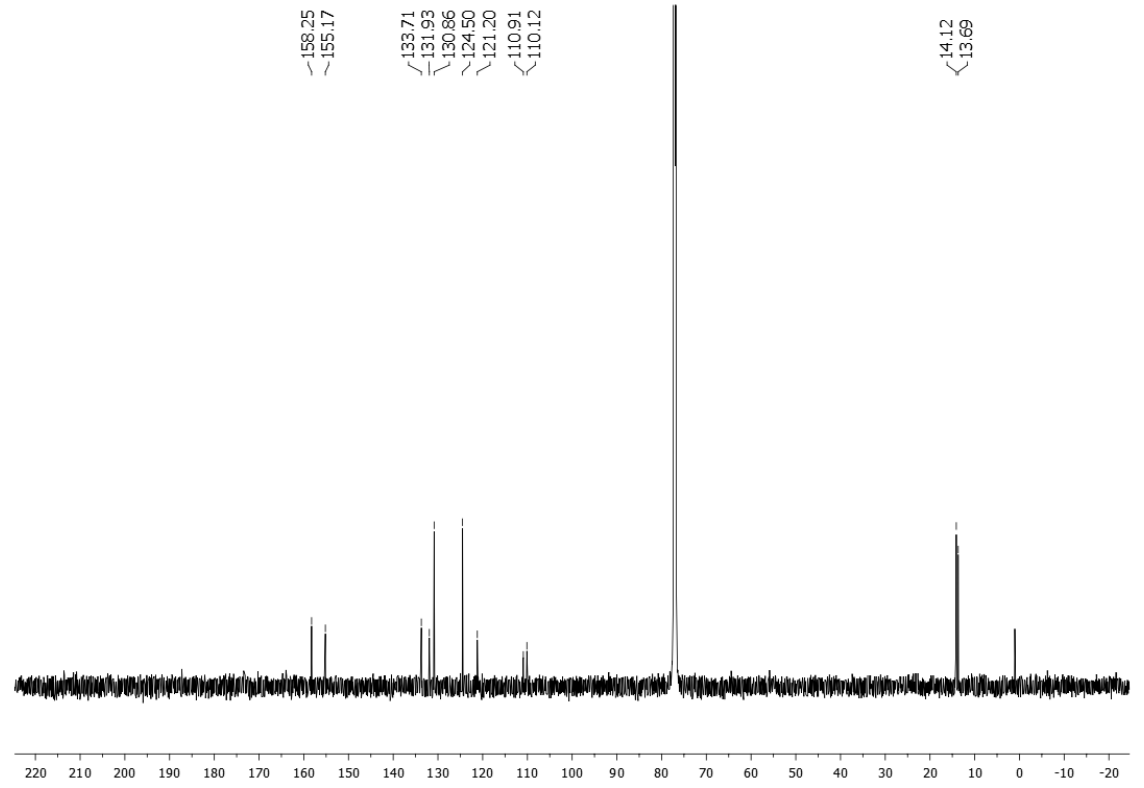
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **3e**



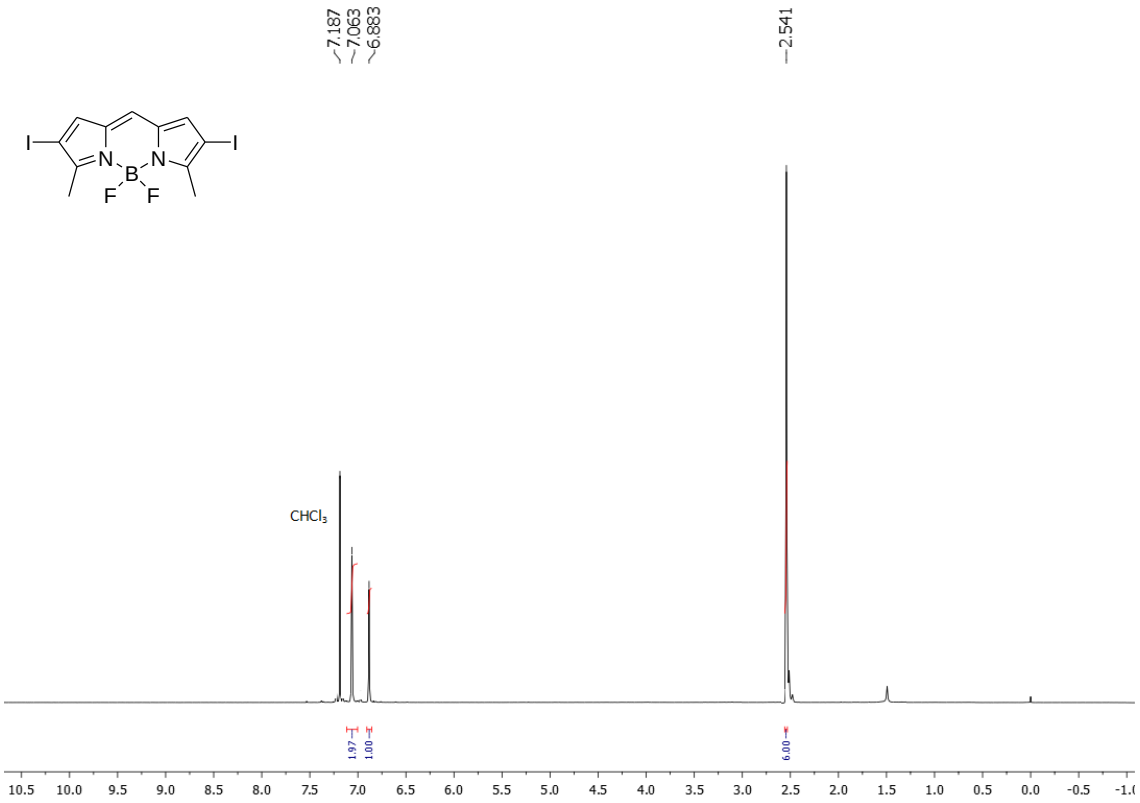


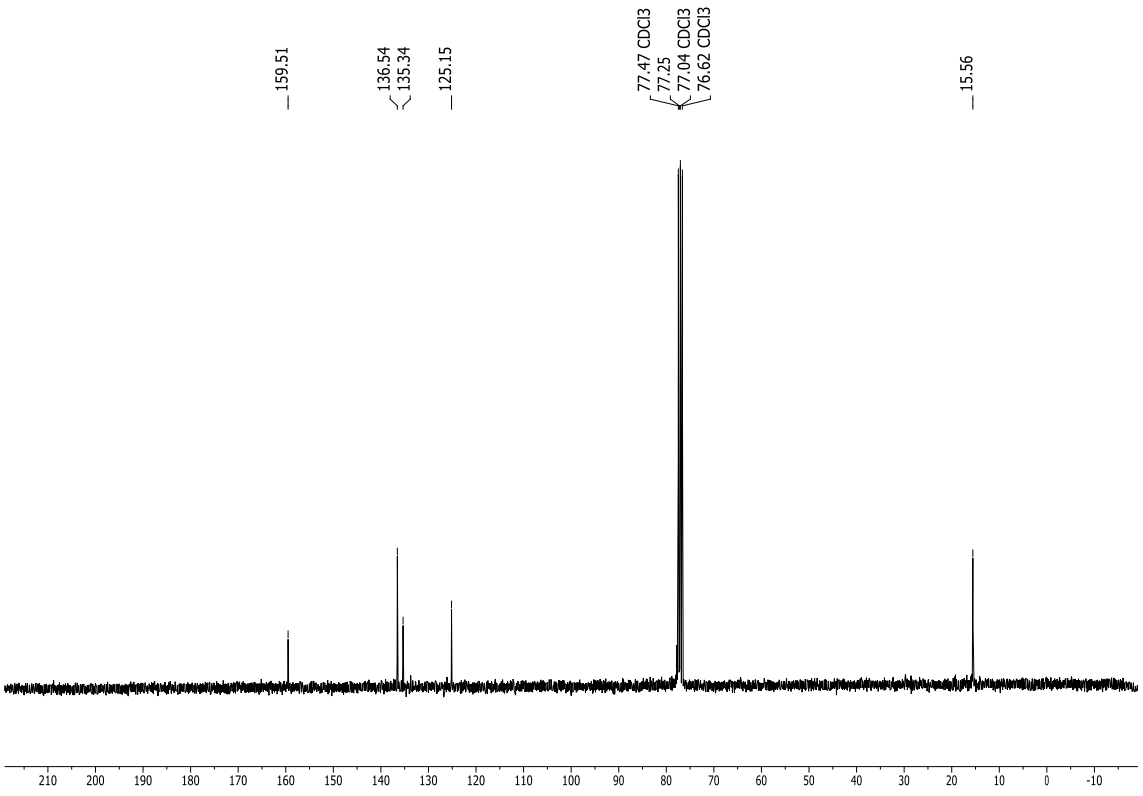
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **14**



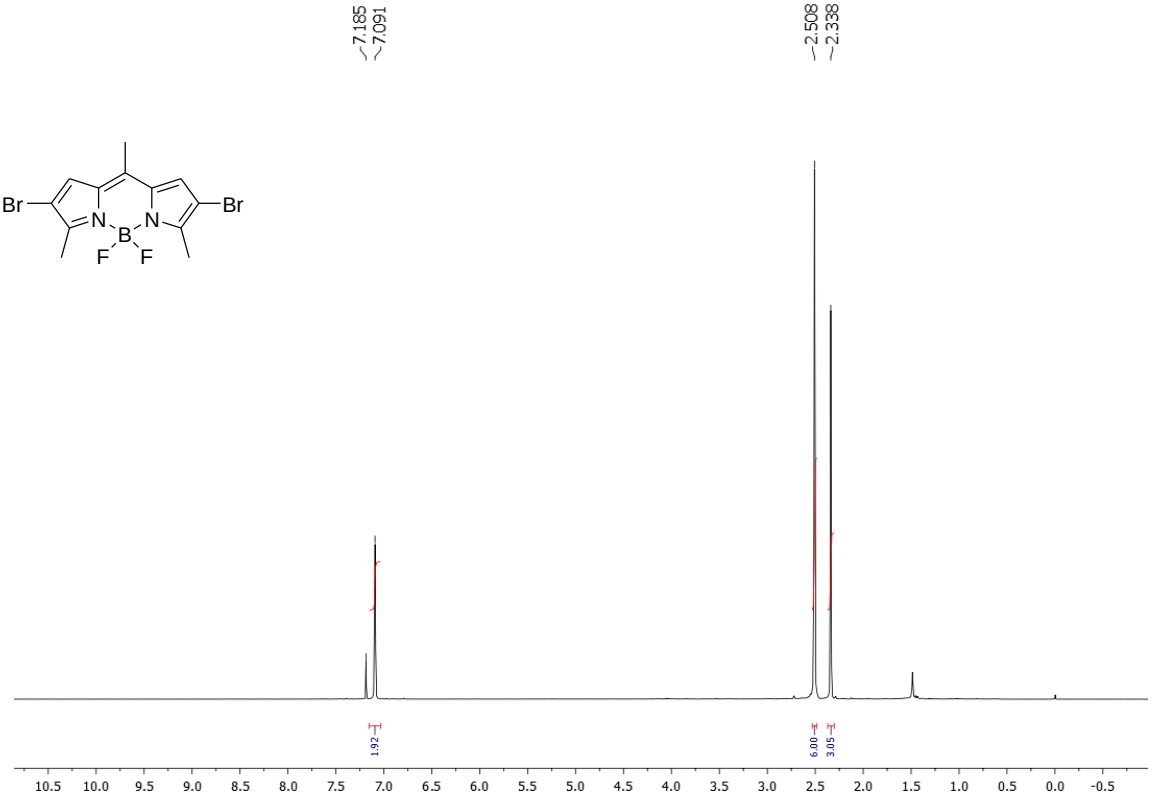


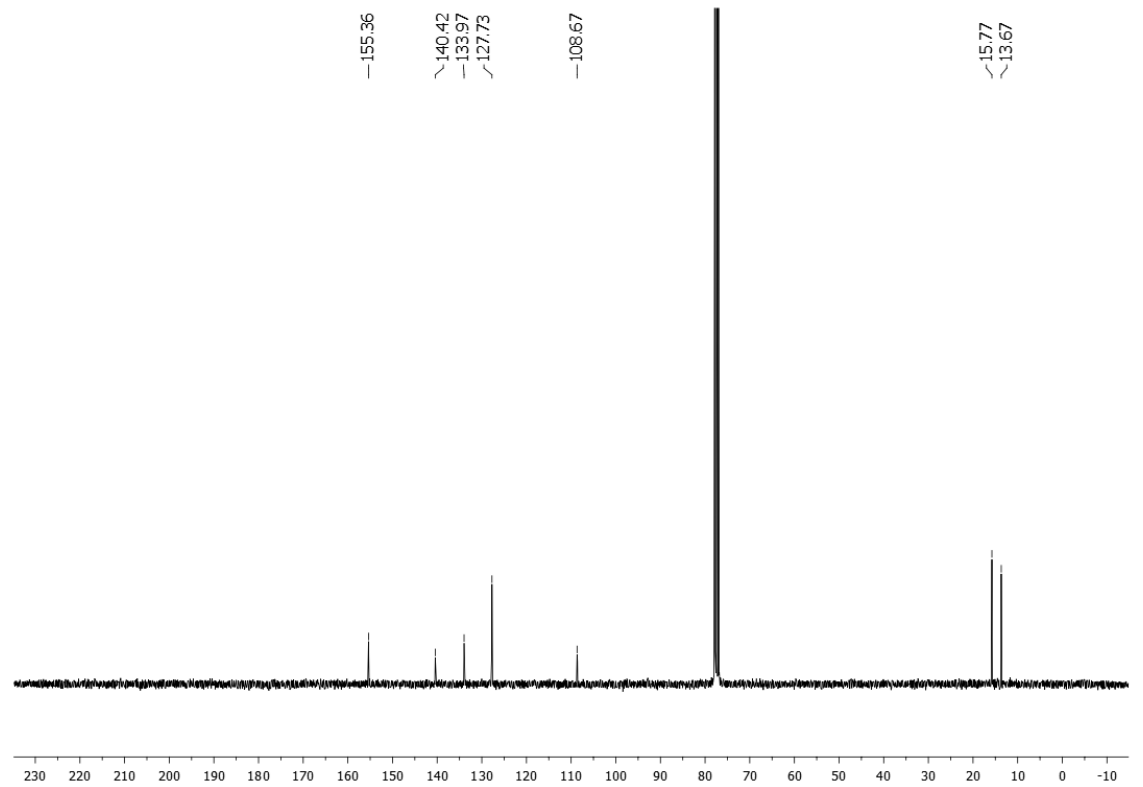
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of **3f**



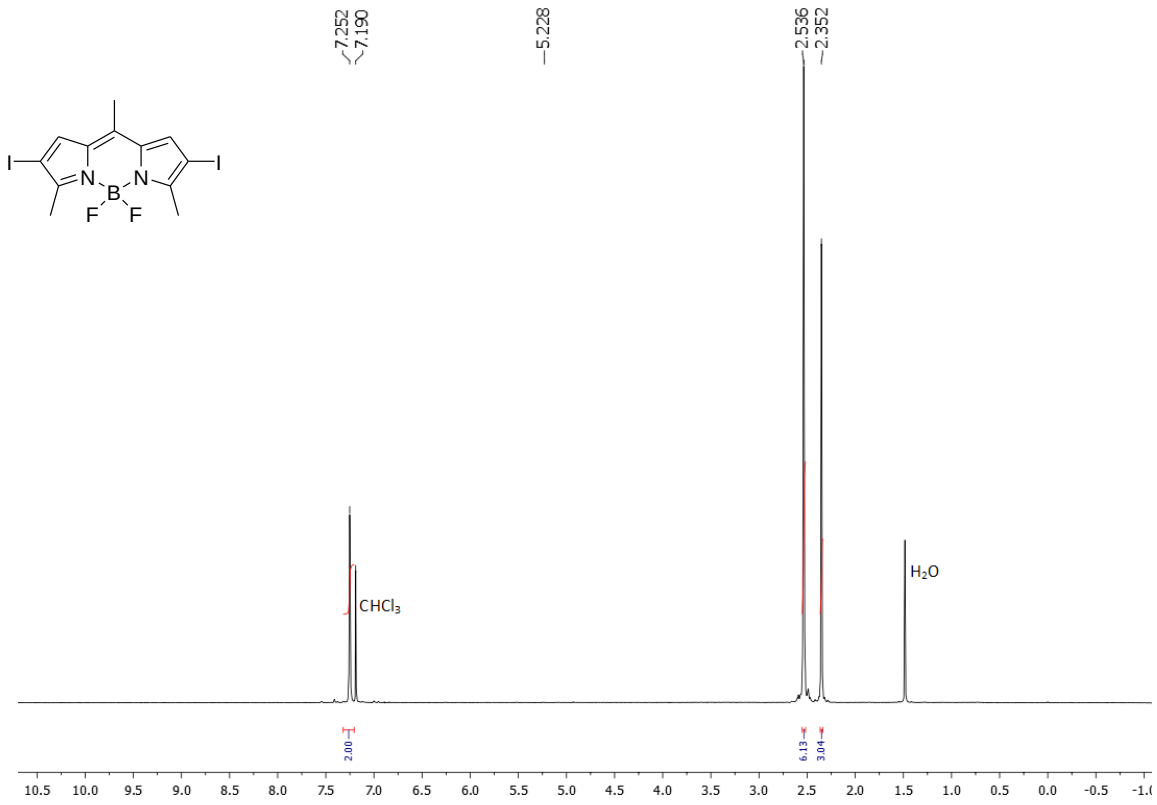


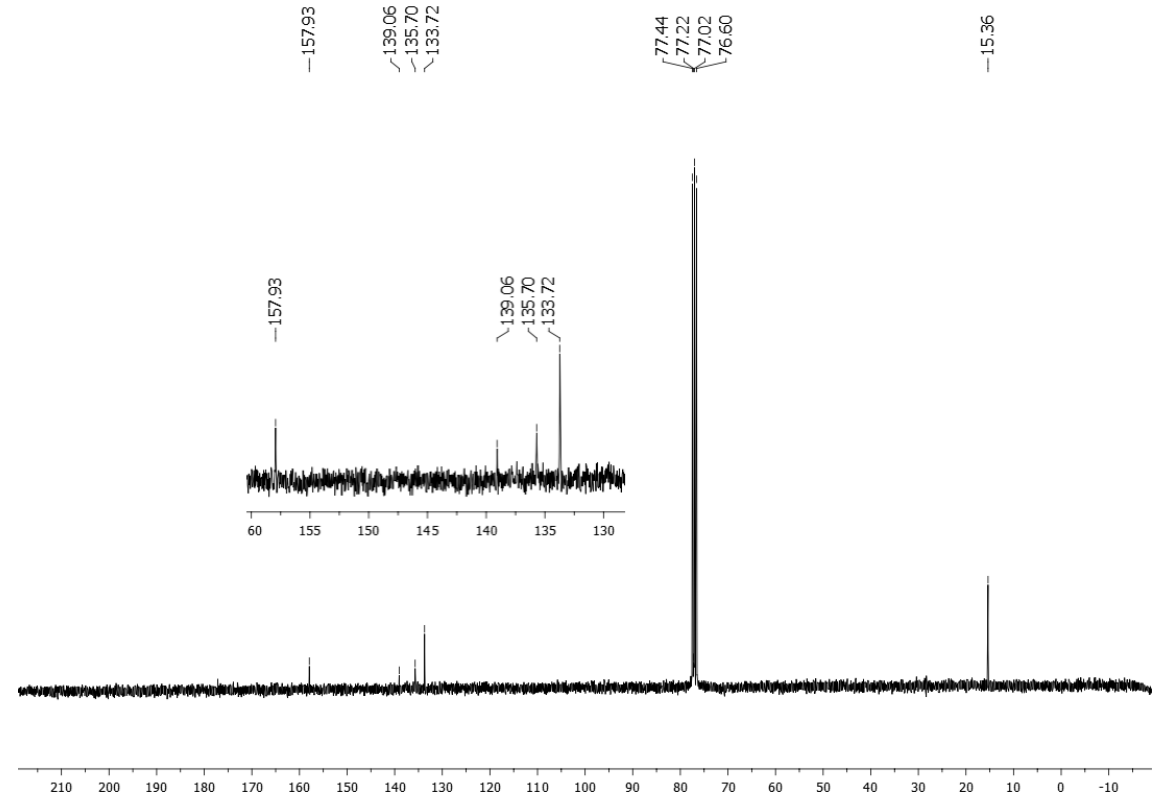
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of **3g**



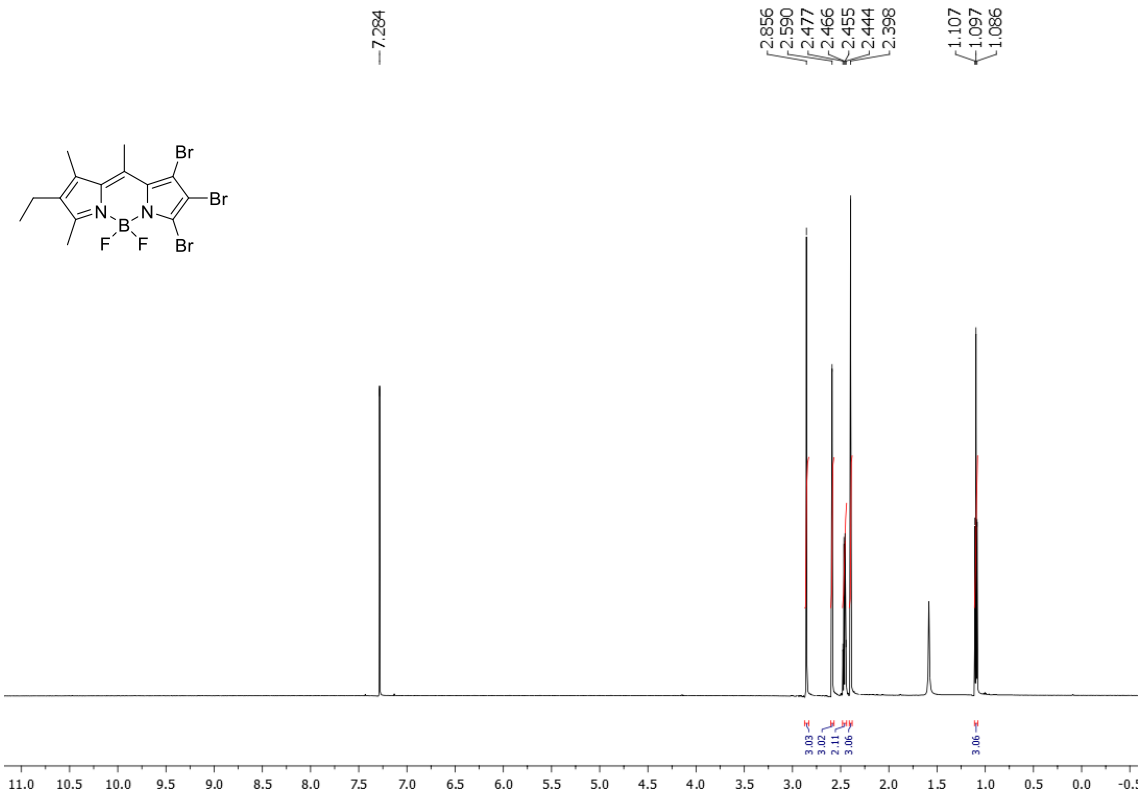


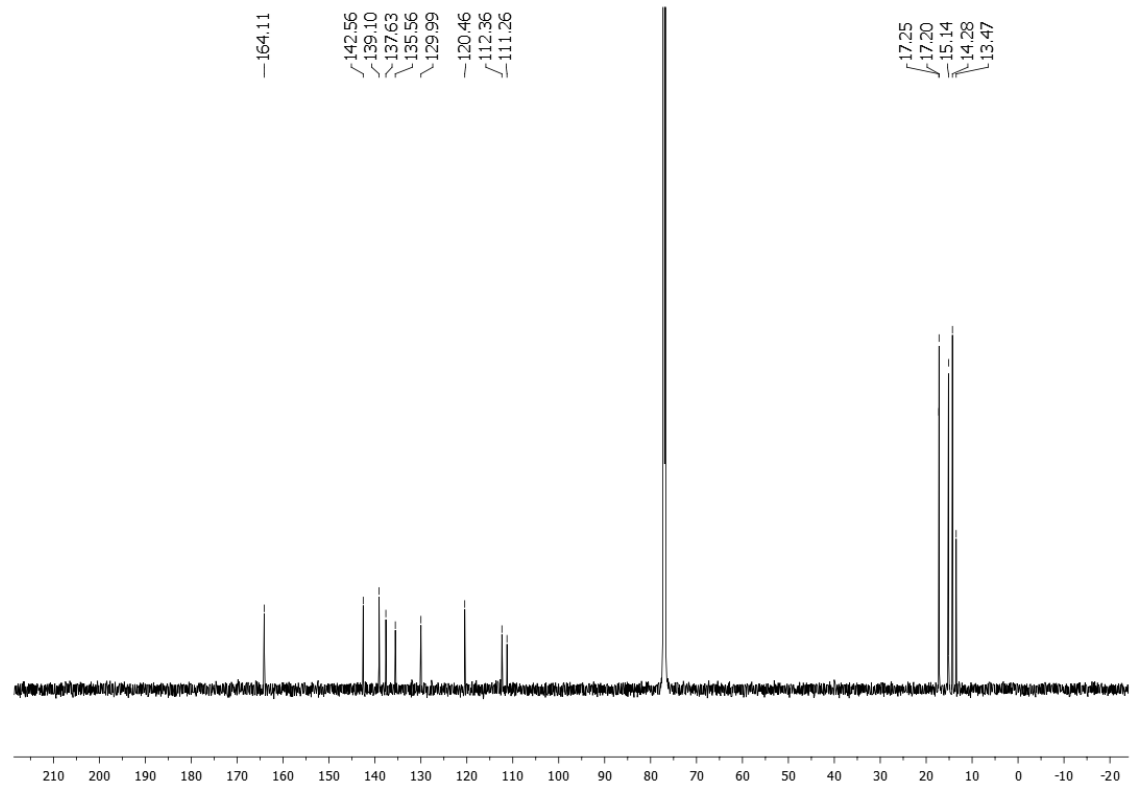
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of **3h**



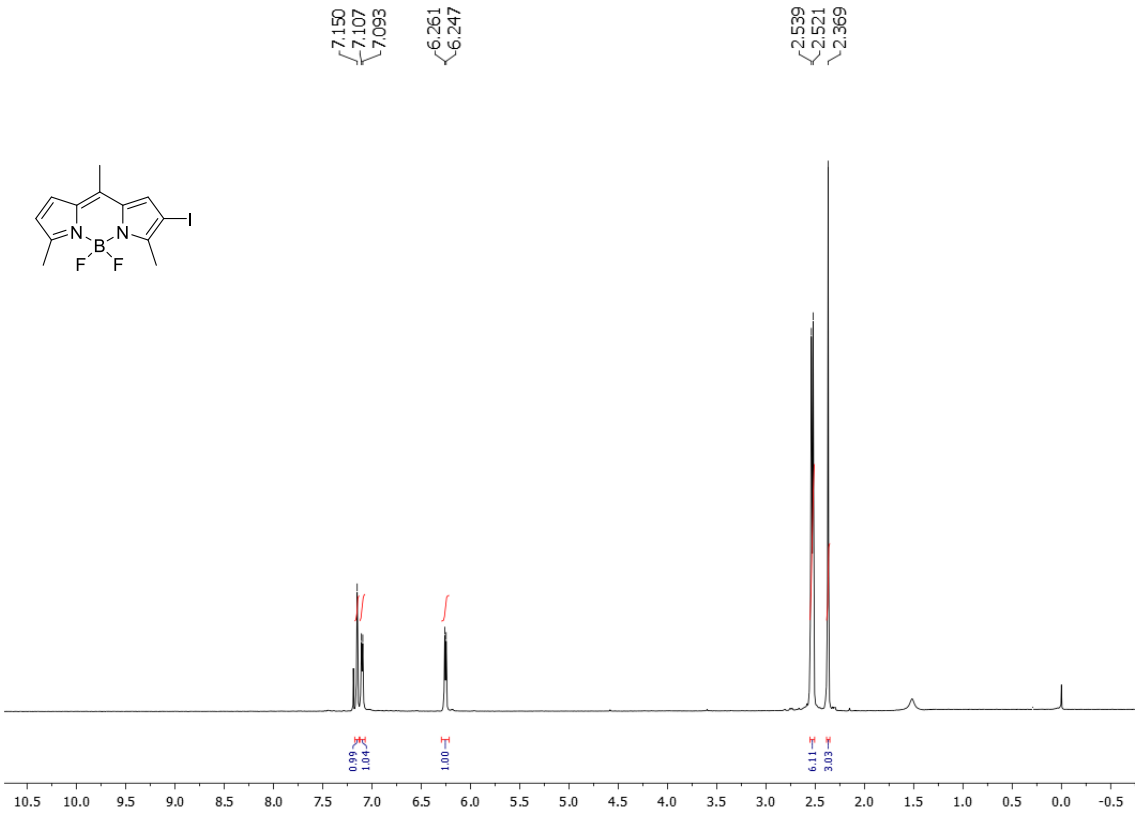


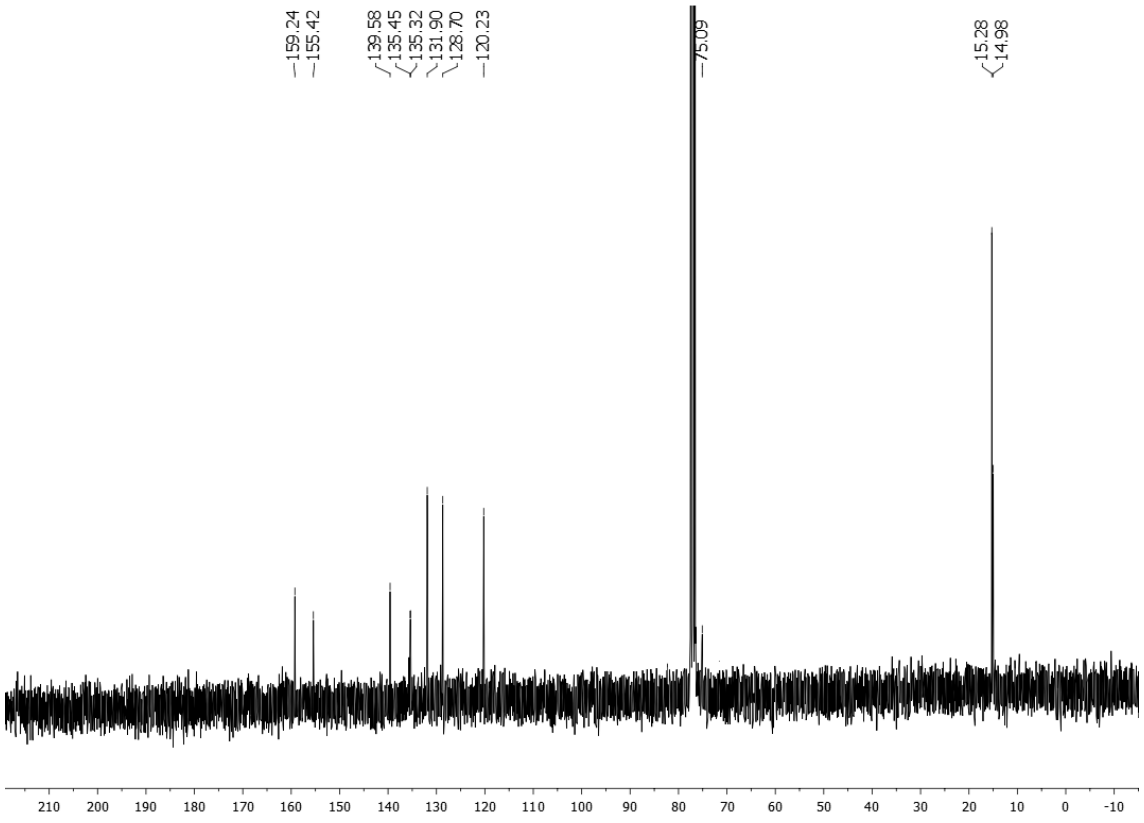
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **13**



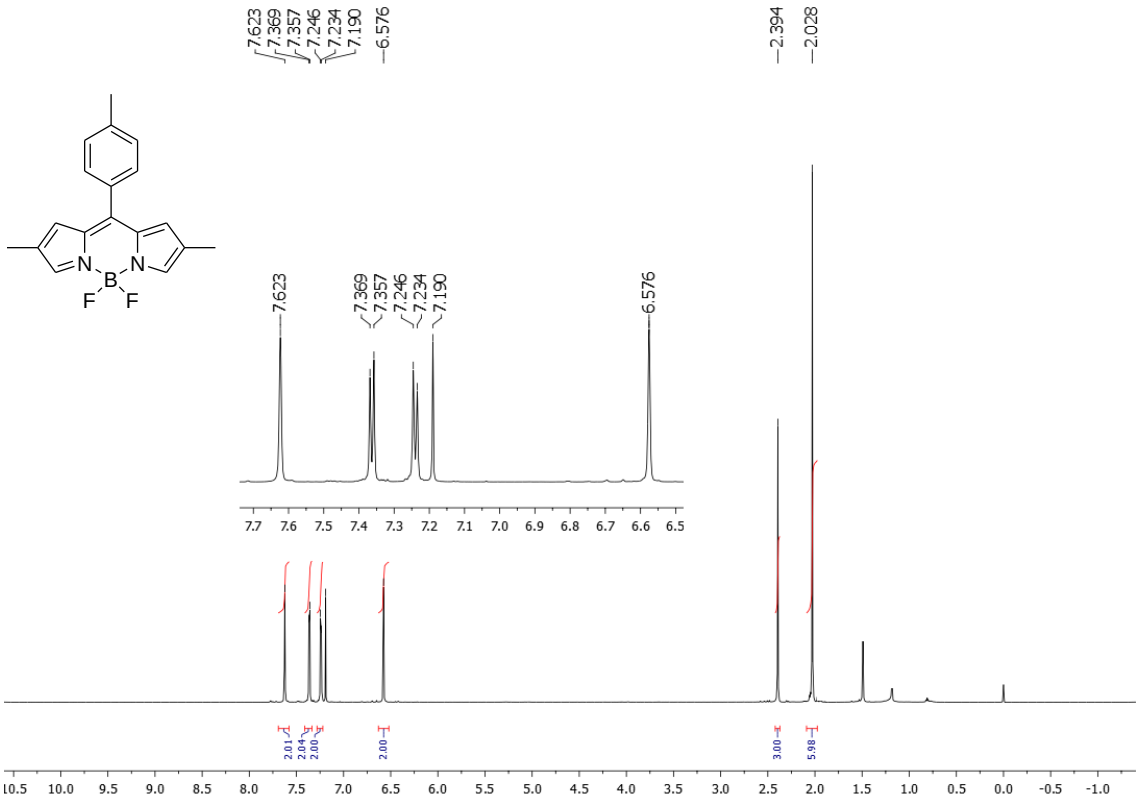


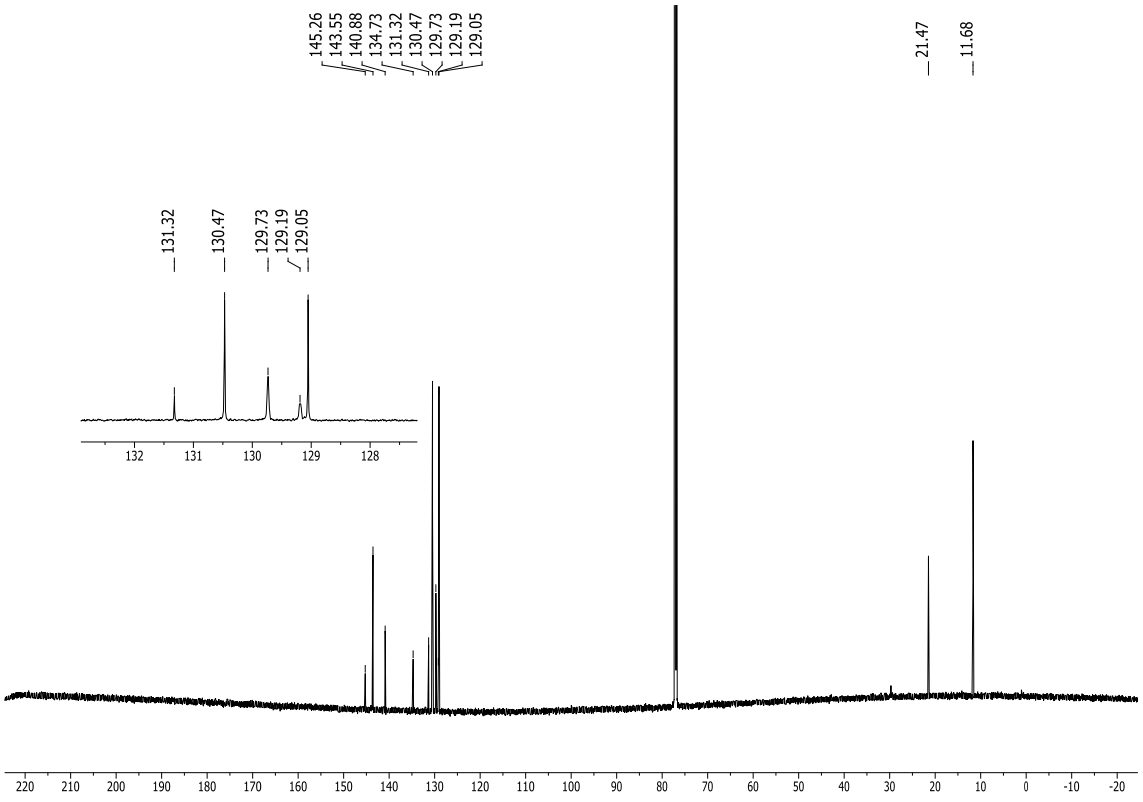
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of **24b**



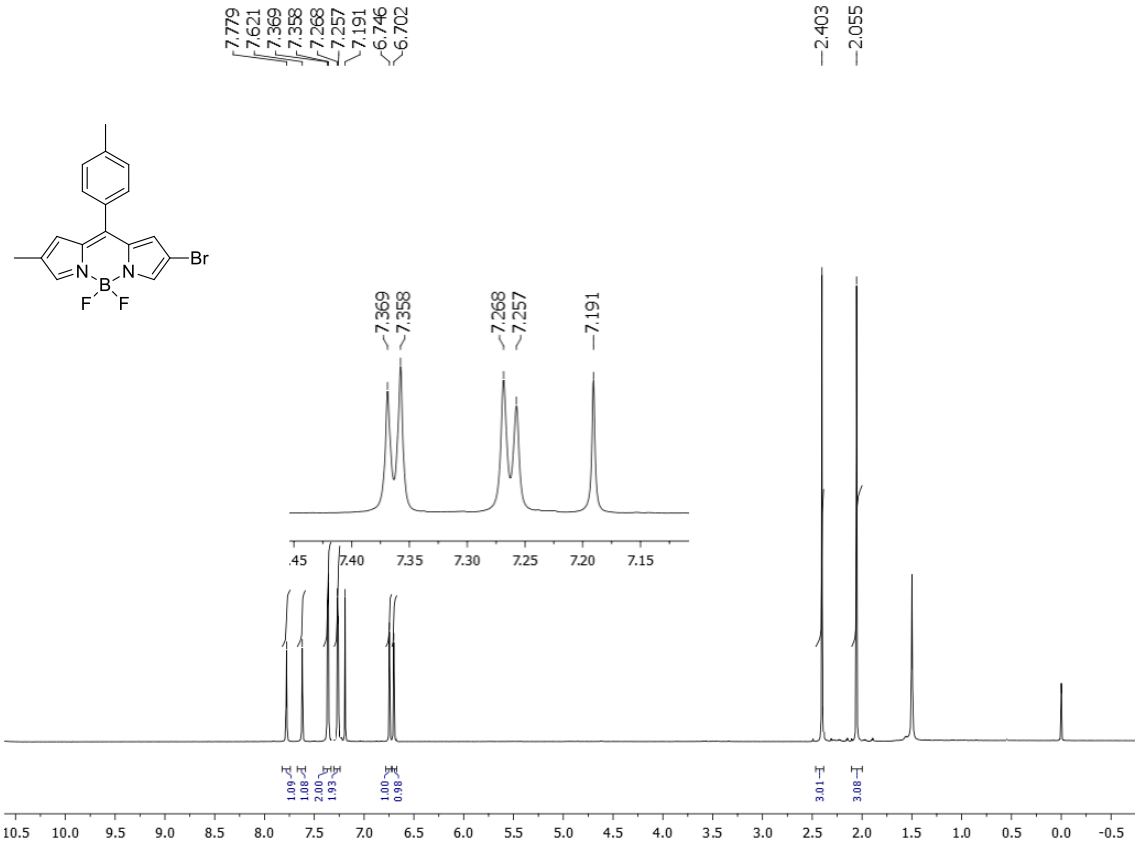


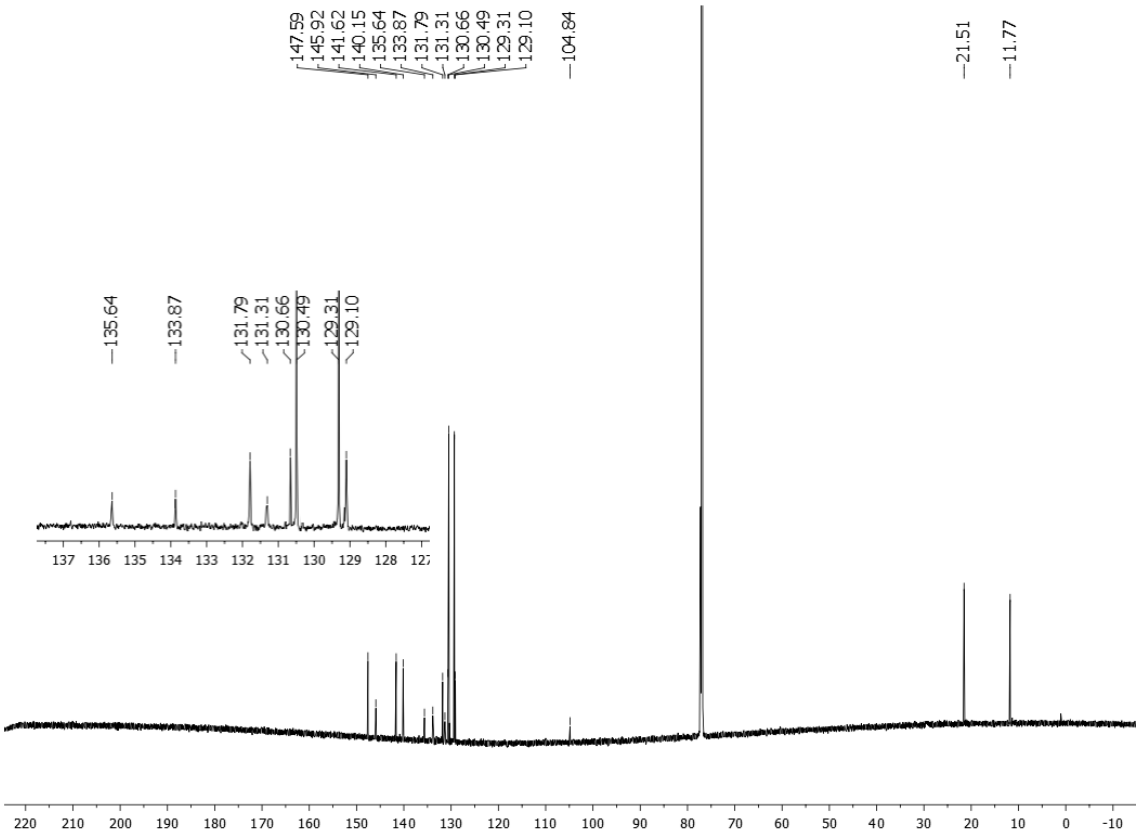
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **4a**



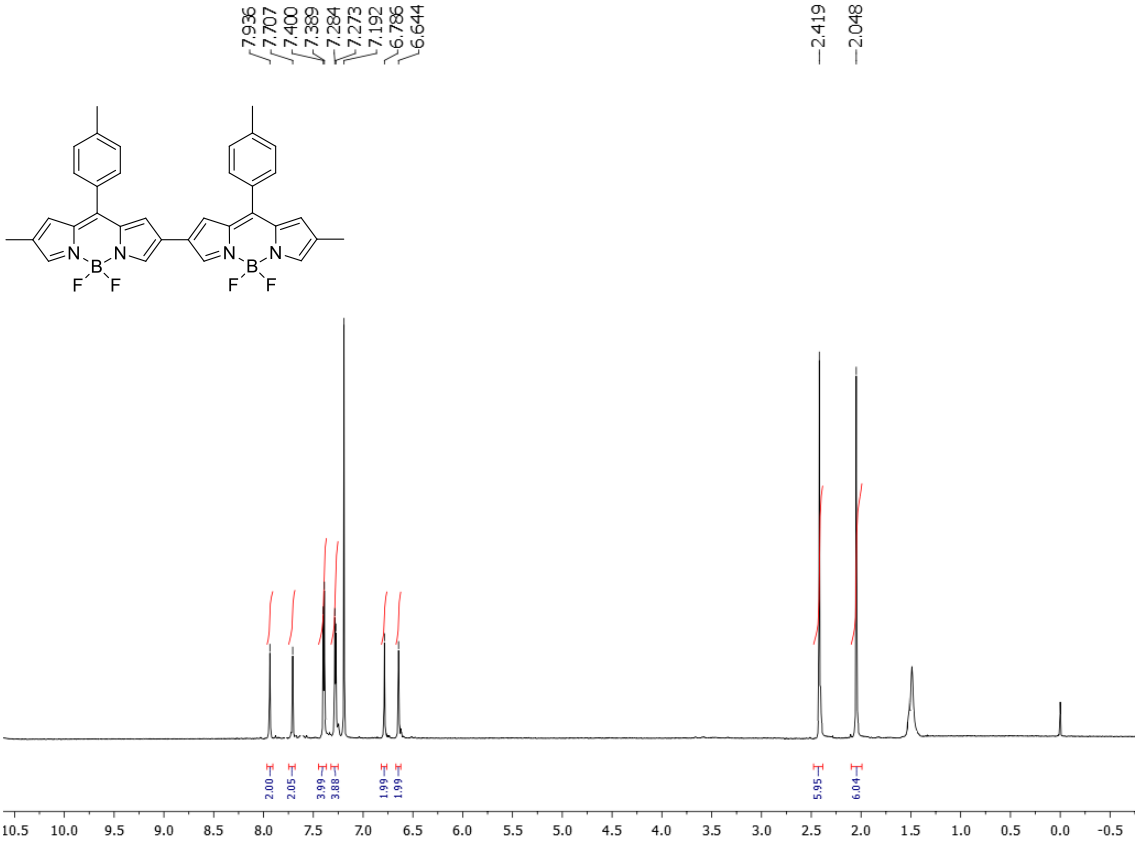


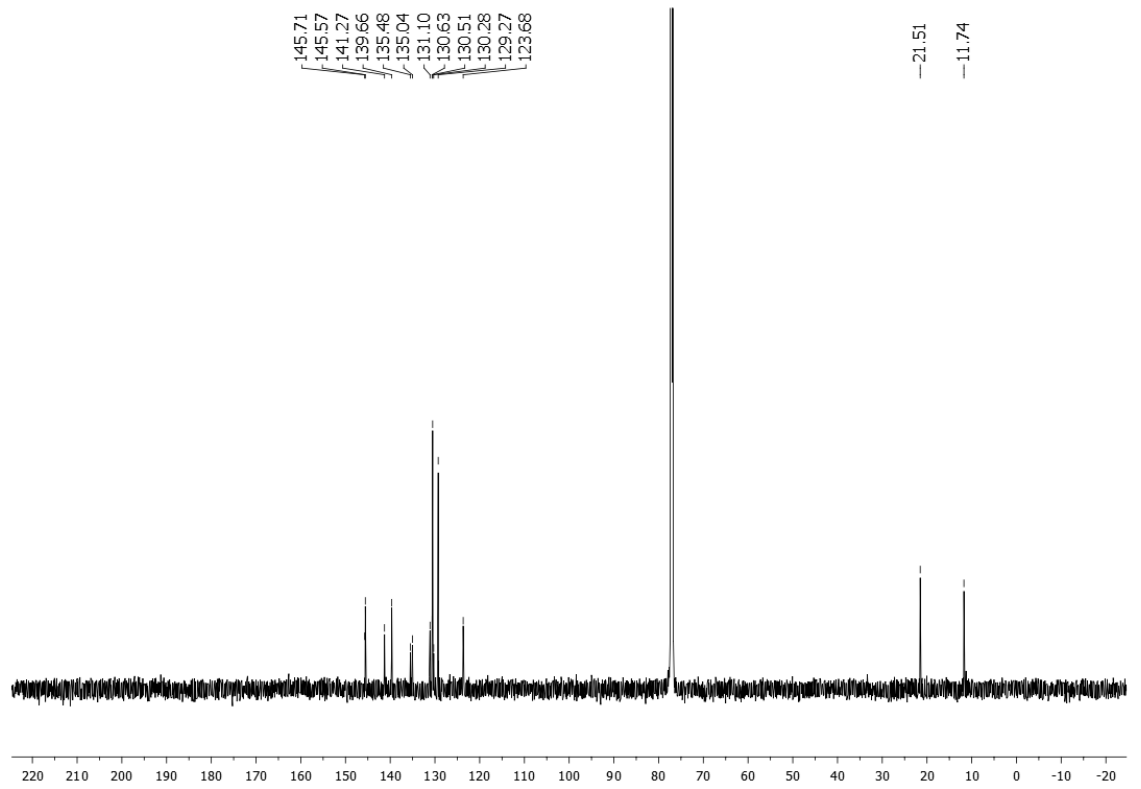
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **5a**



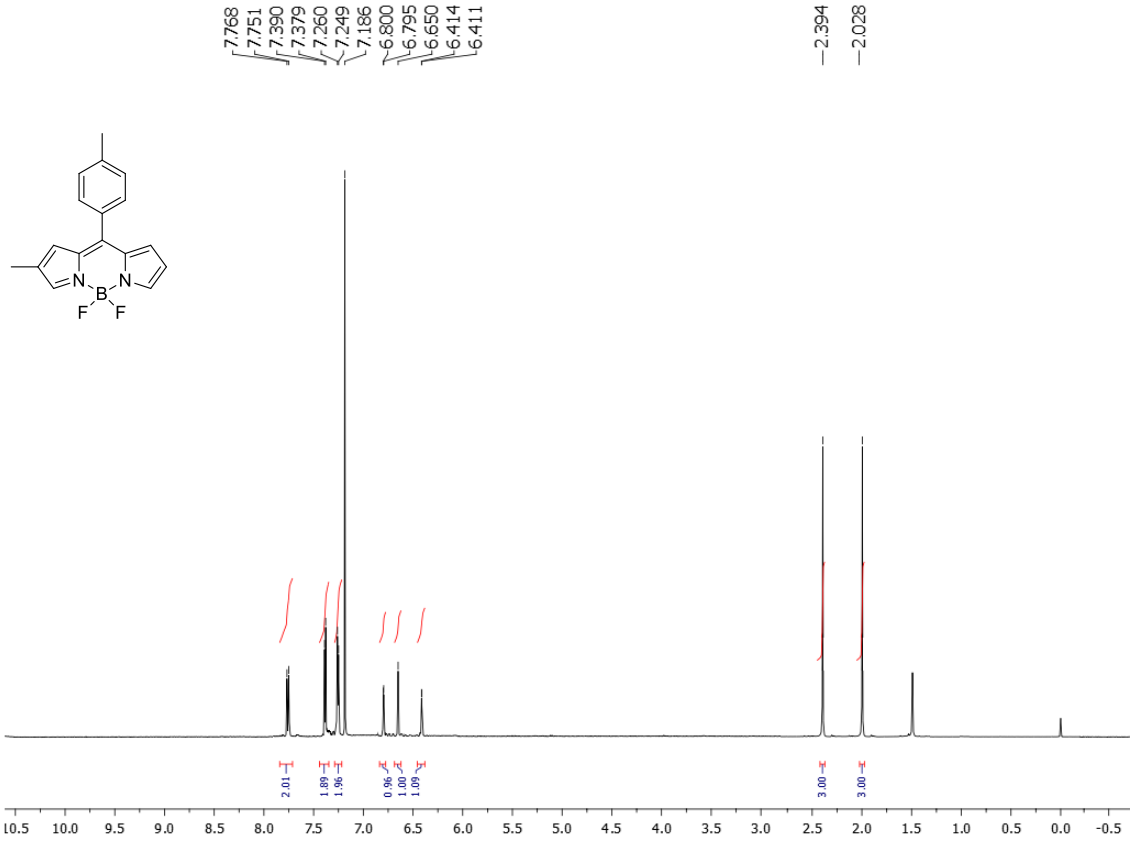


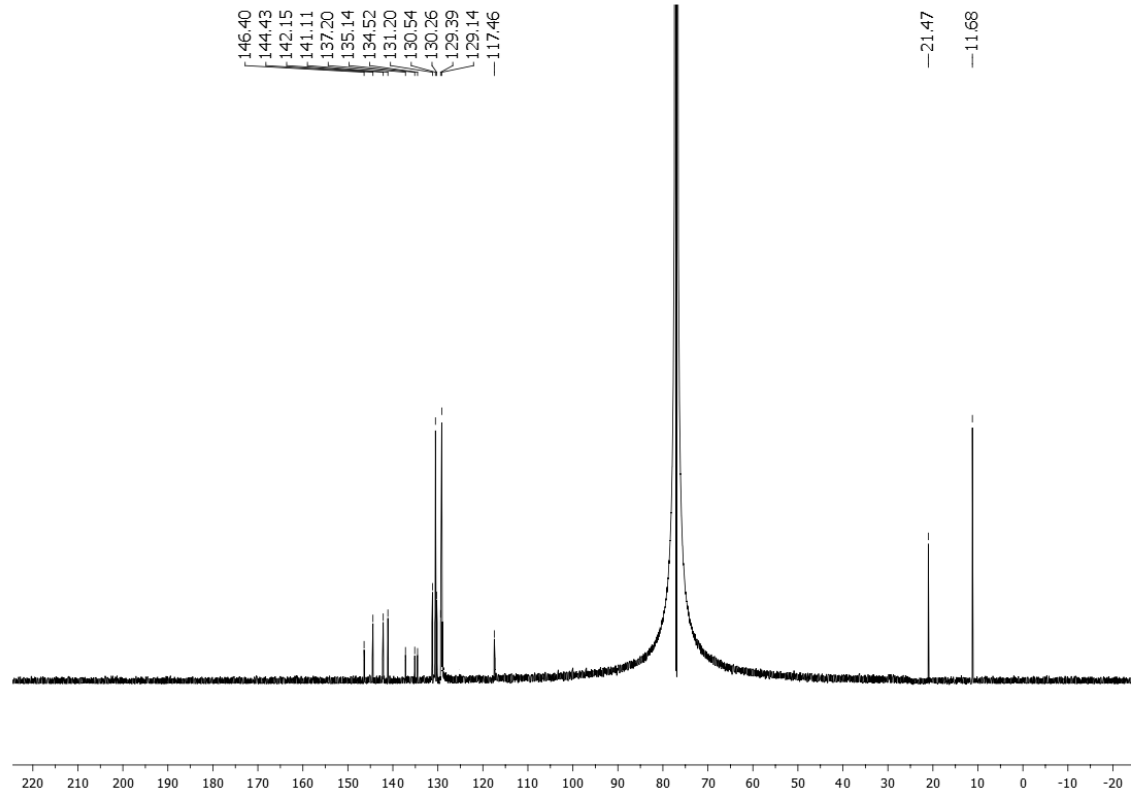
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **6**



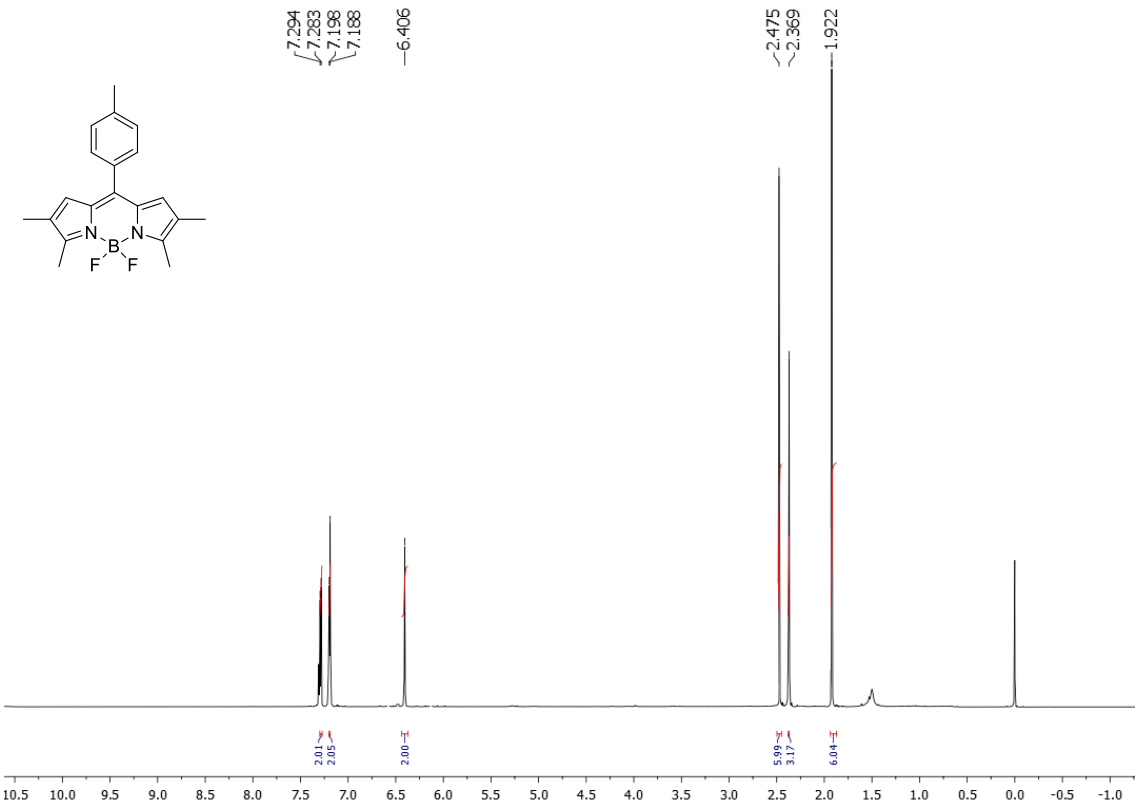


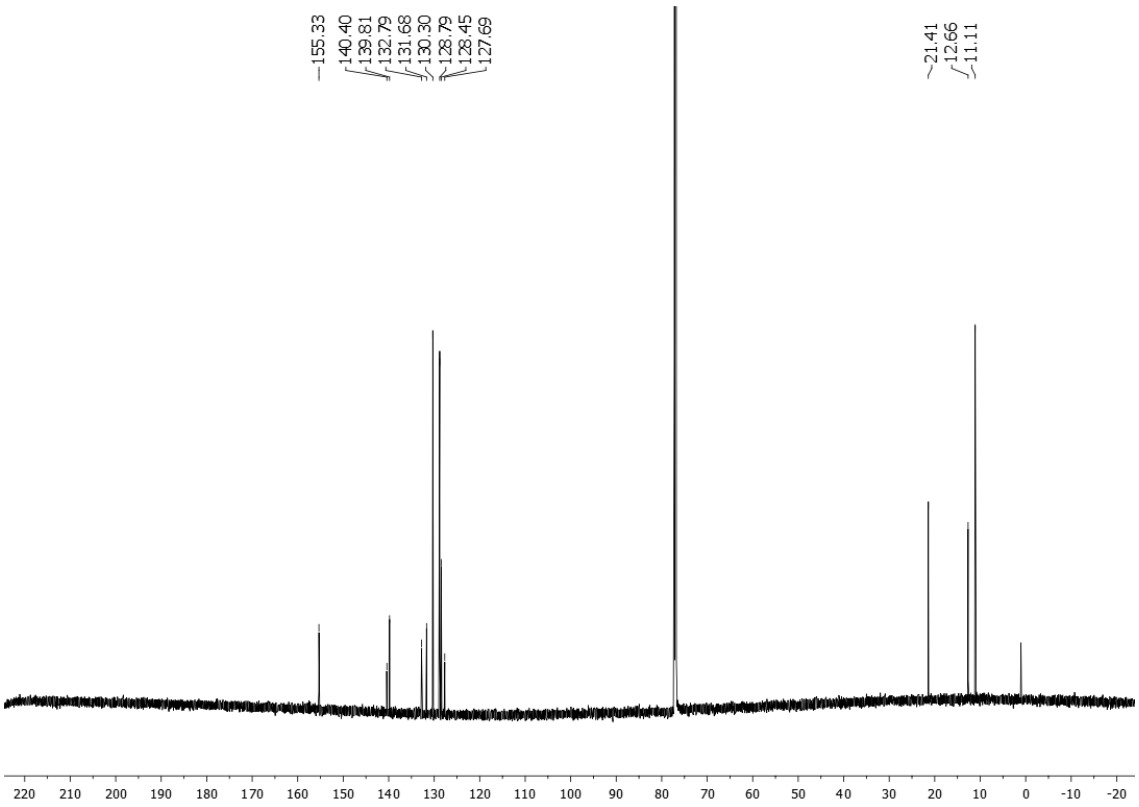
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **7a**



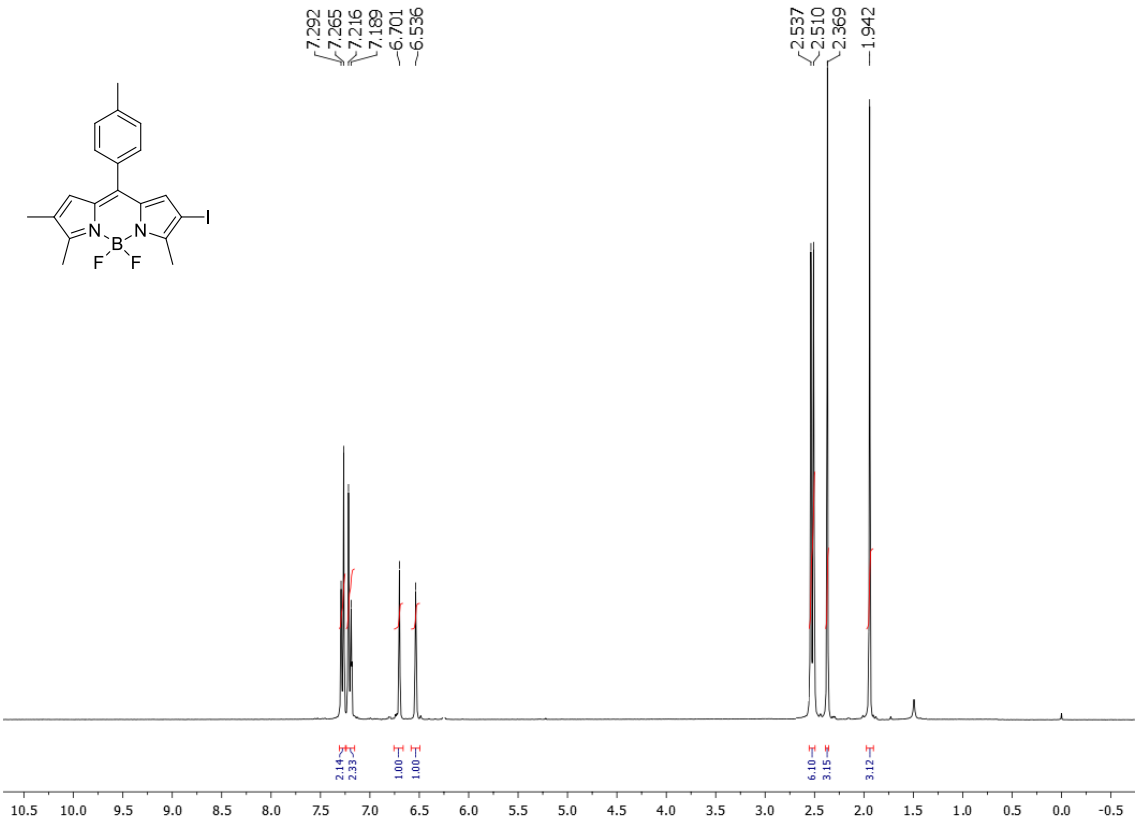


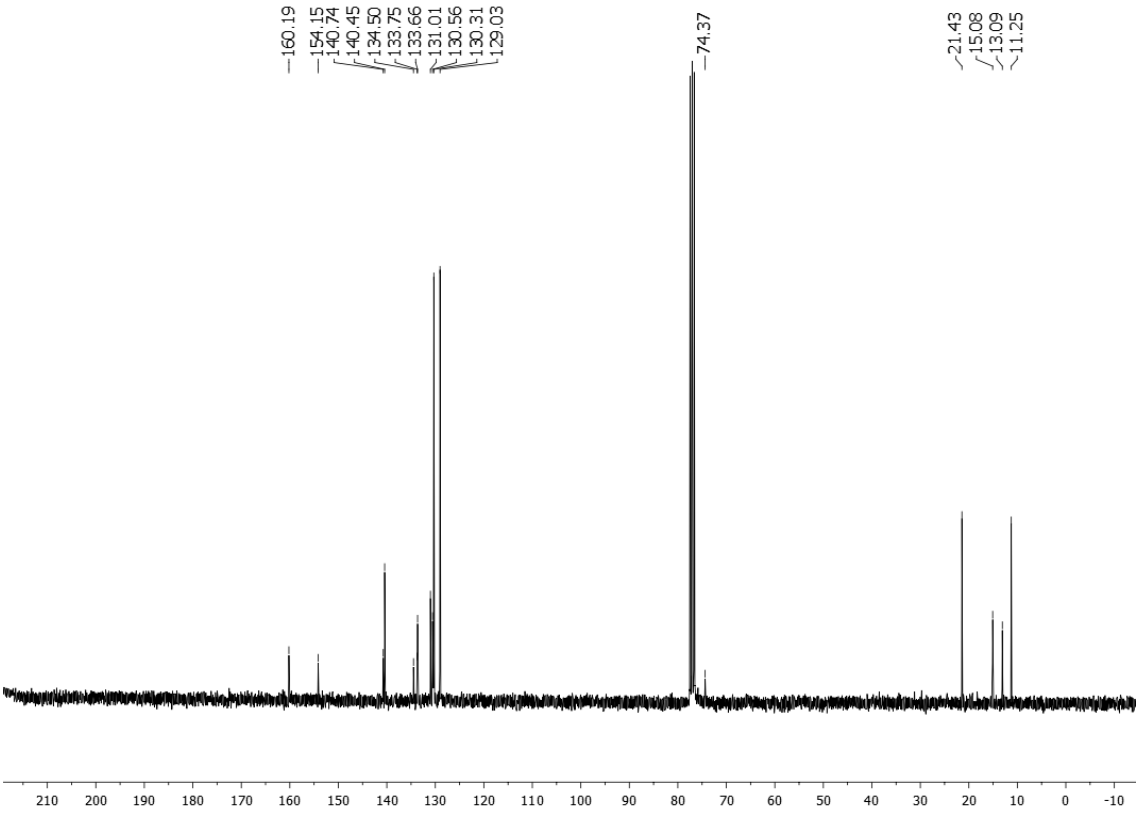
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **4b**



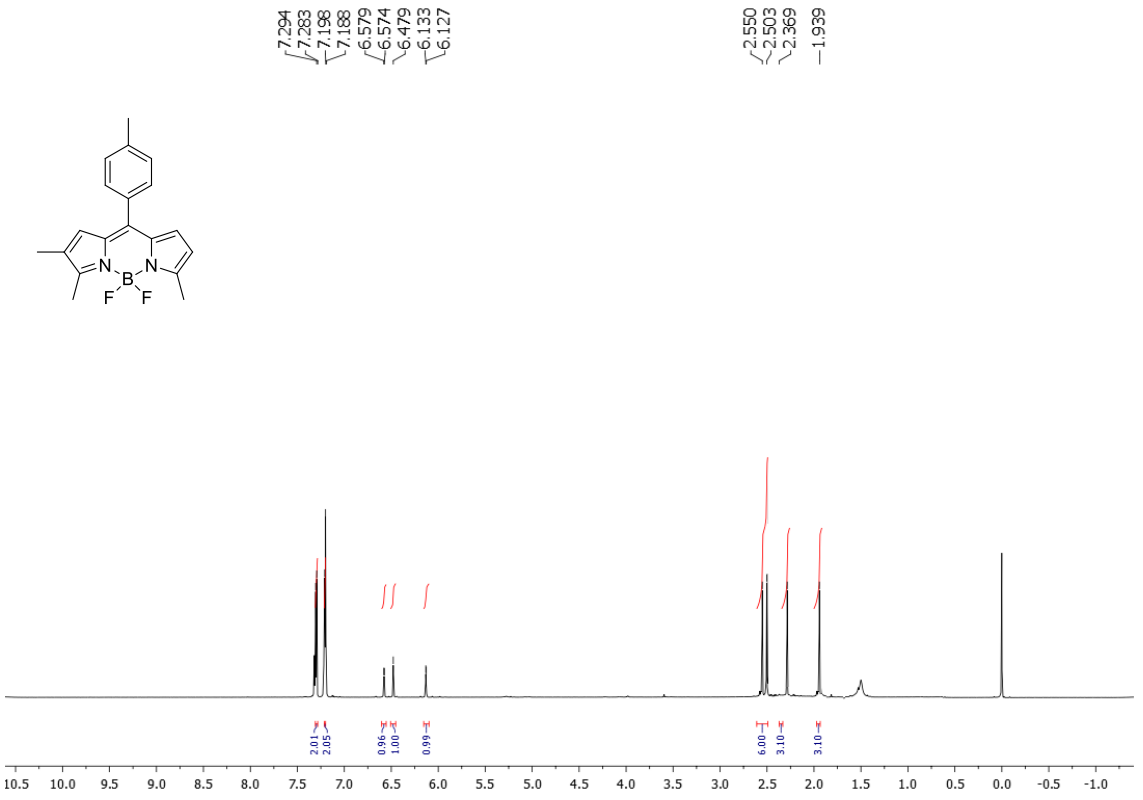


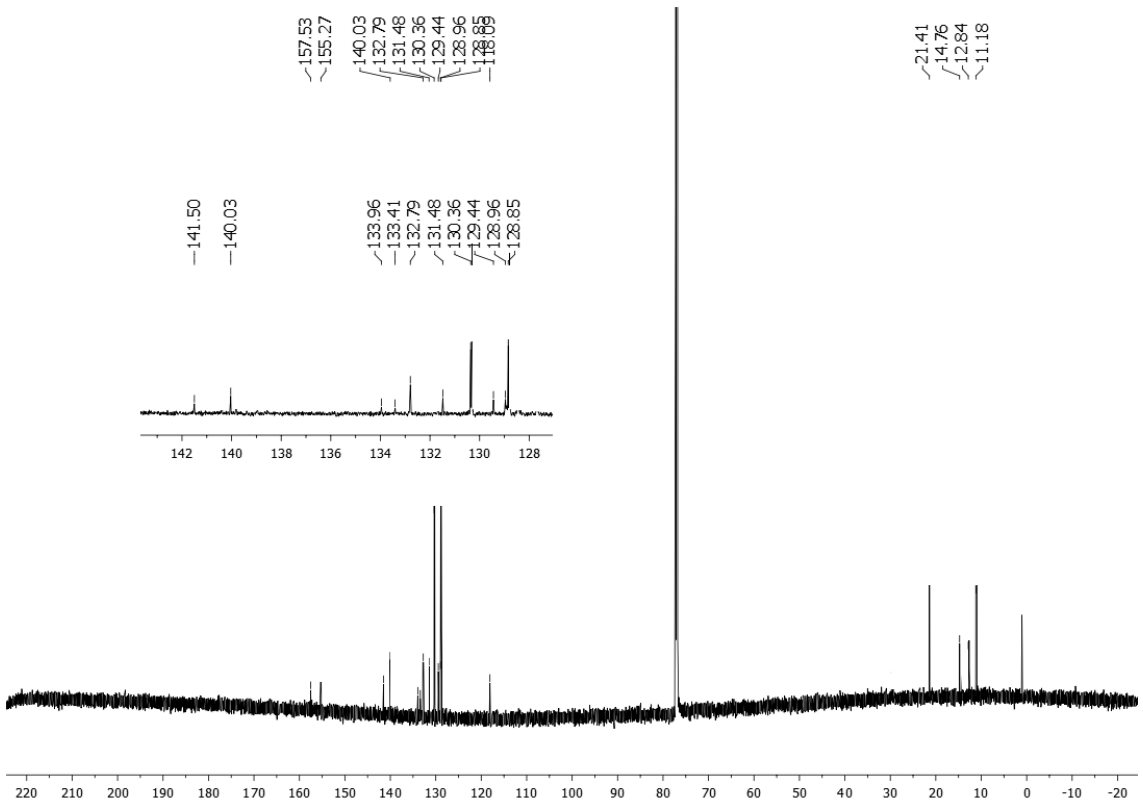
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of **5b**



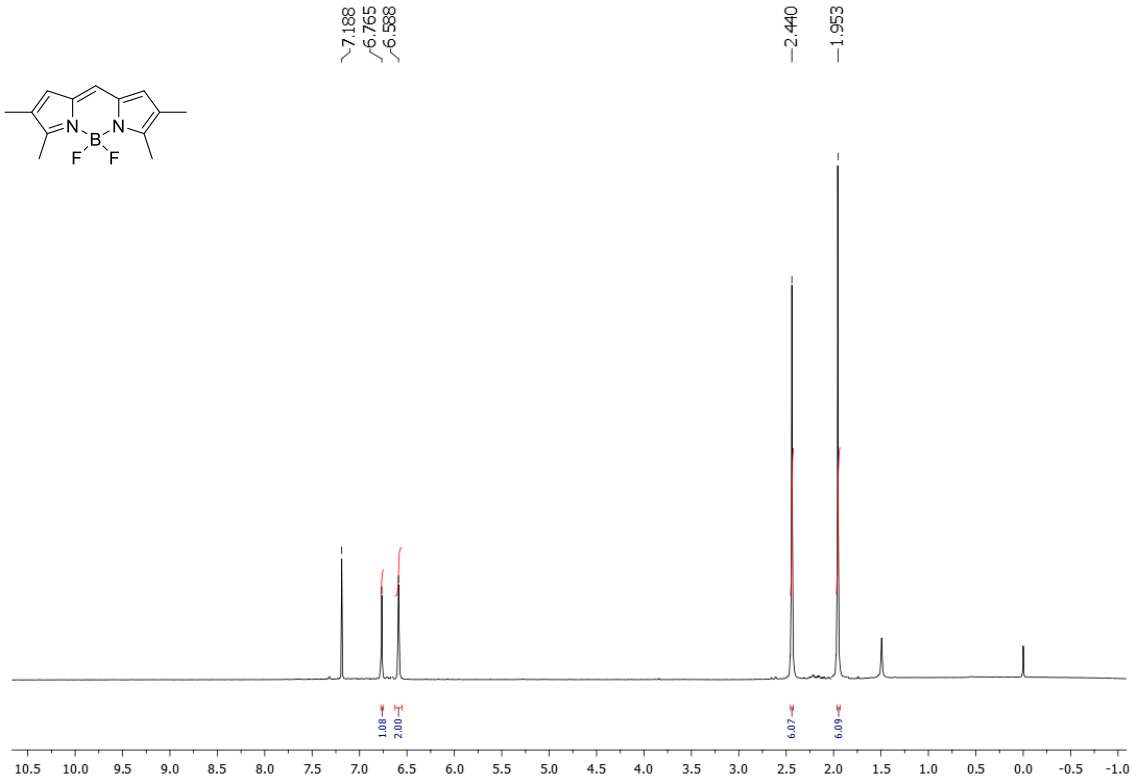


^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **7b**

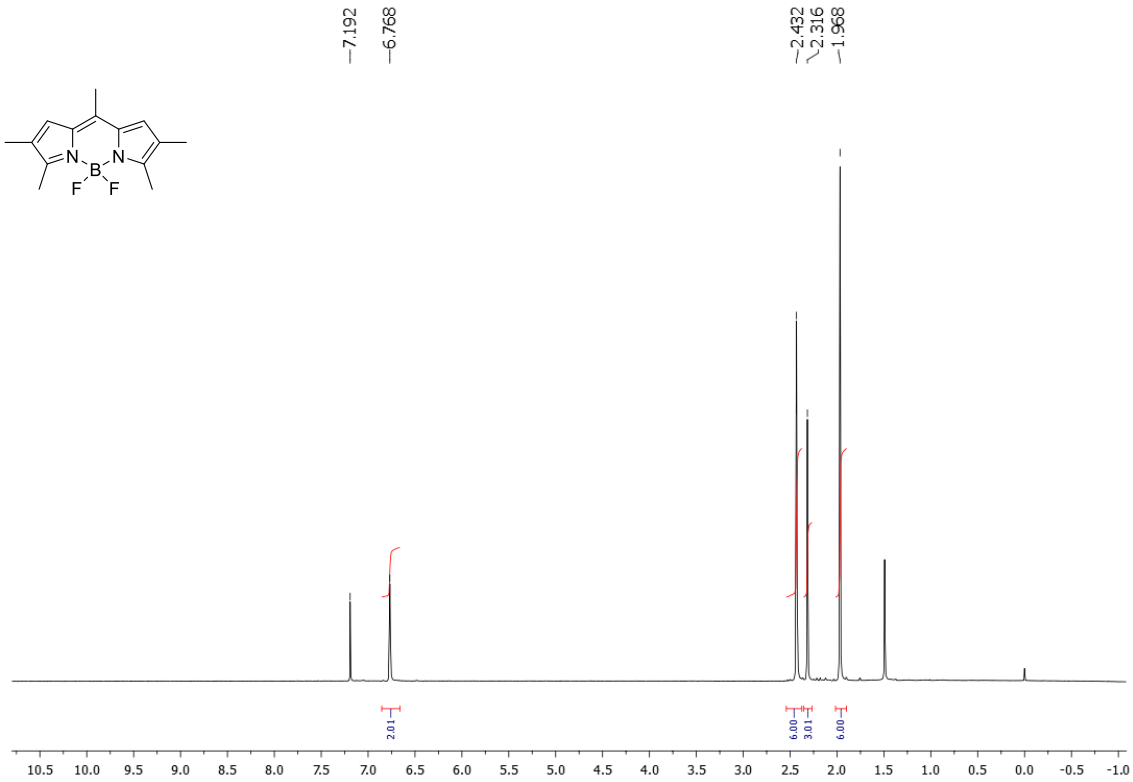




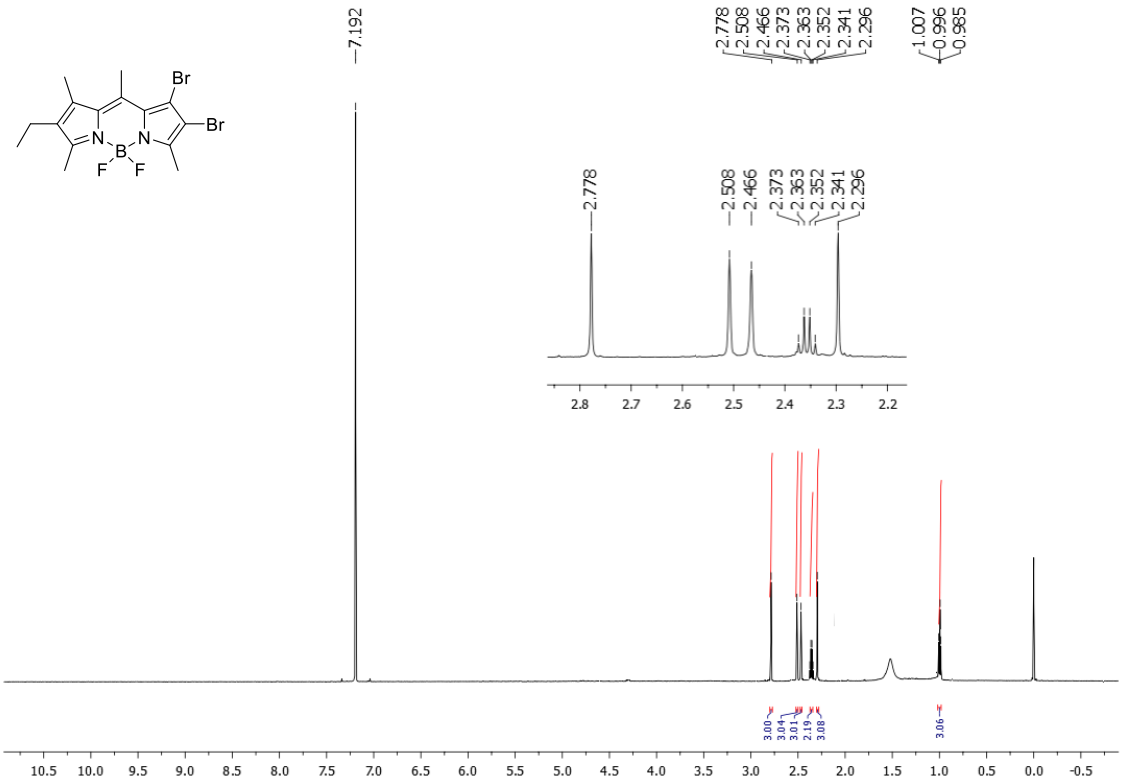
^{1}H (300 MHz, $CDCl_3$) NMR spectrum of known **4c**[1]

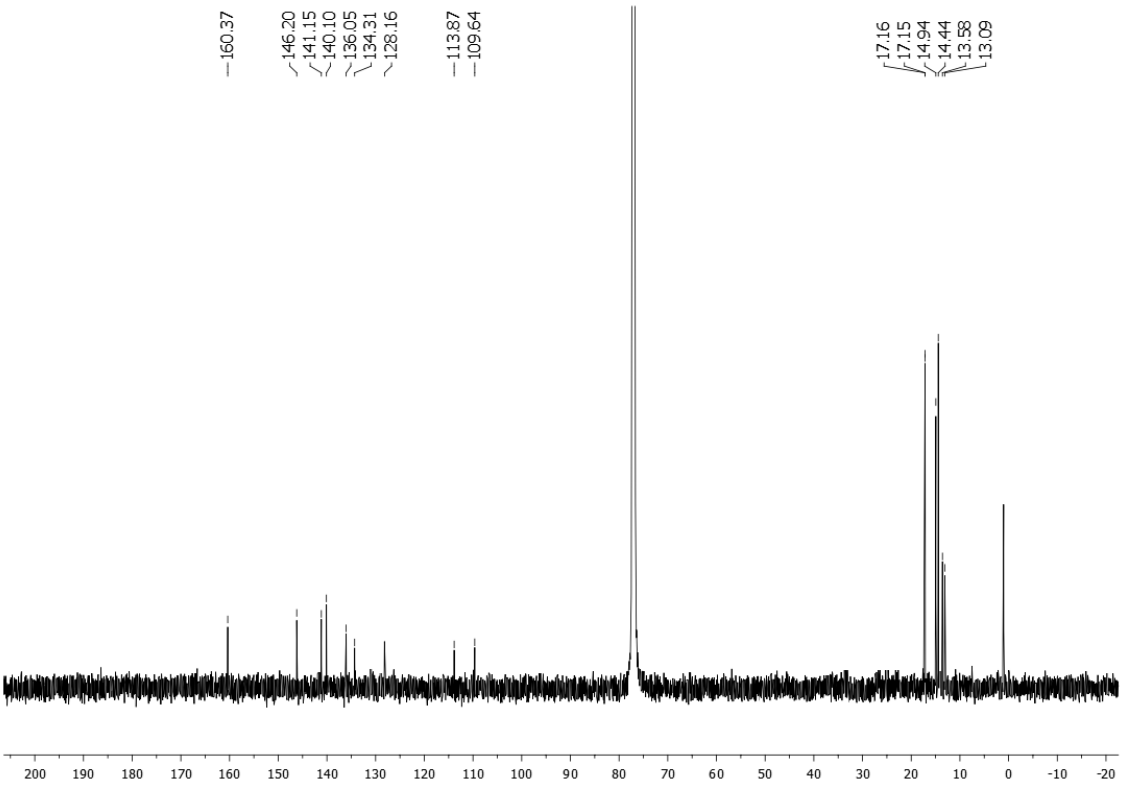


^{1}H (300 MHz, $CDCl_3$) NMR spectrum of known **4d**[1]

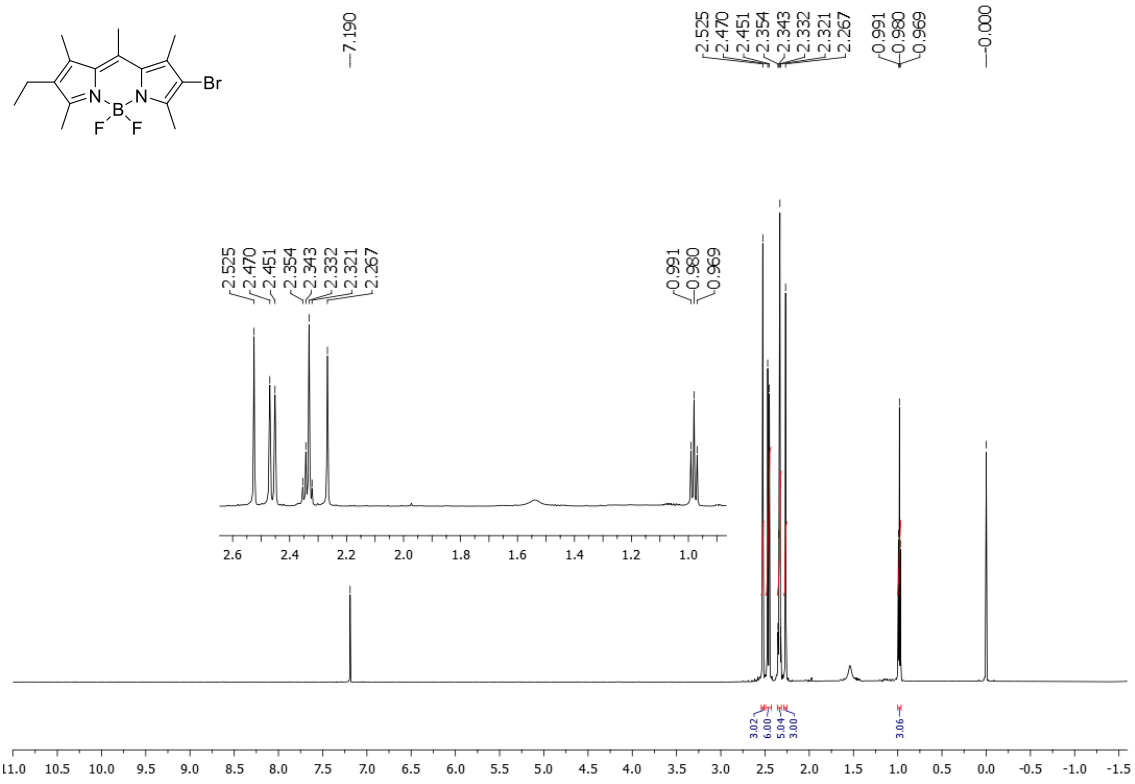


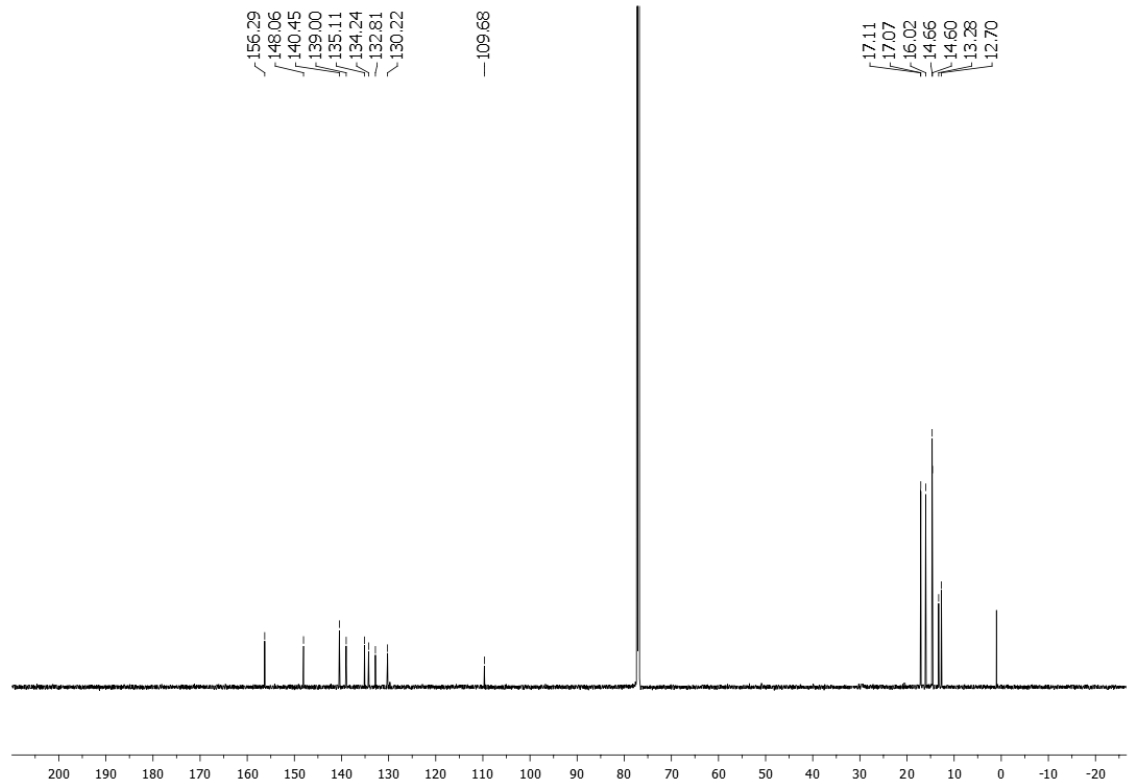
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **16**



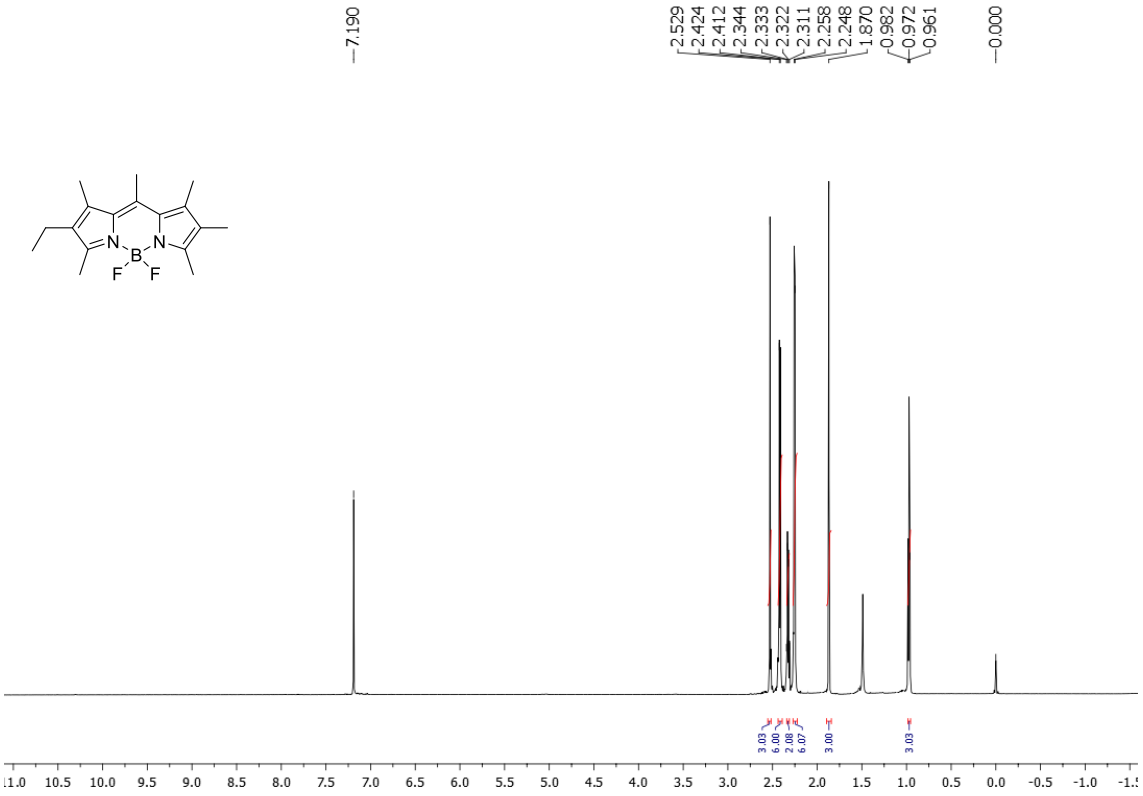


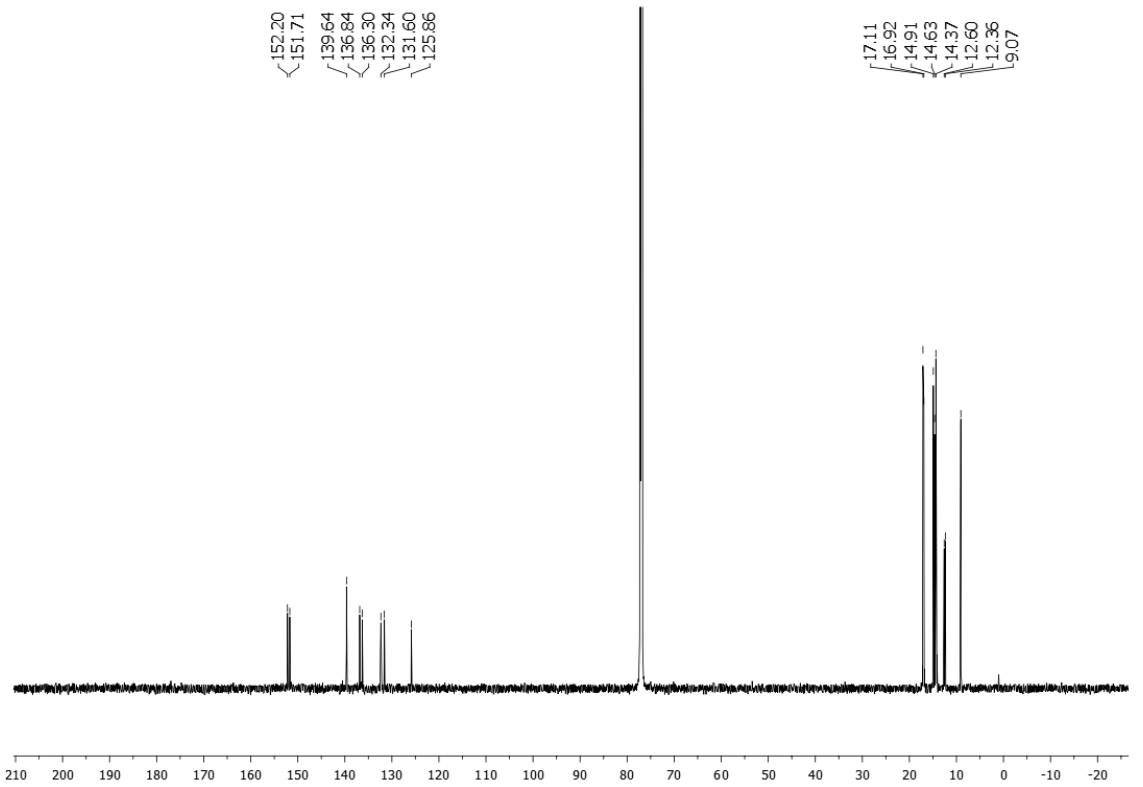
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **17**



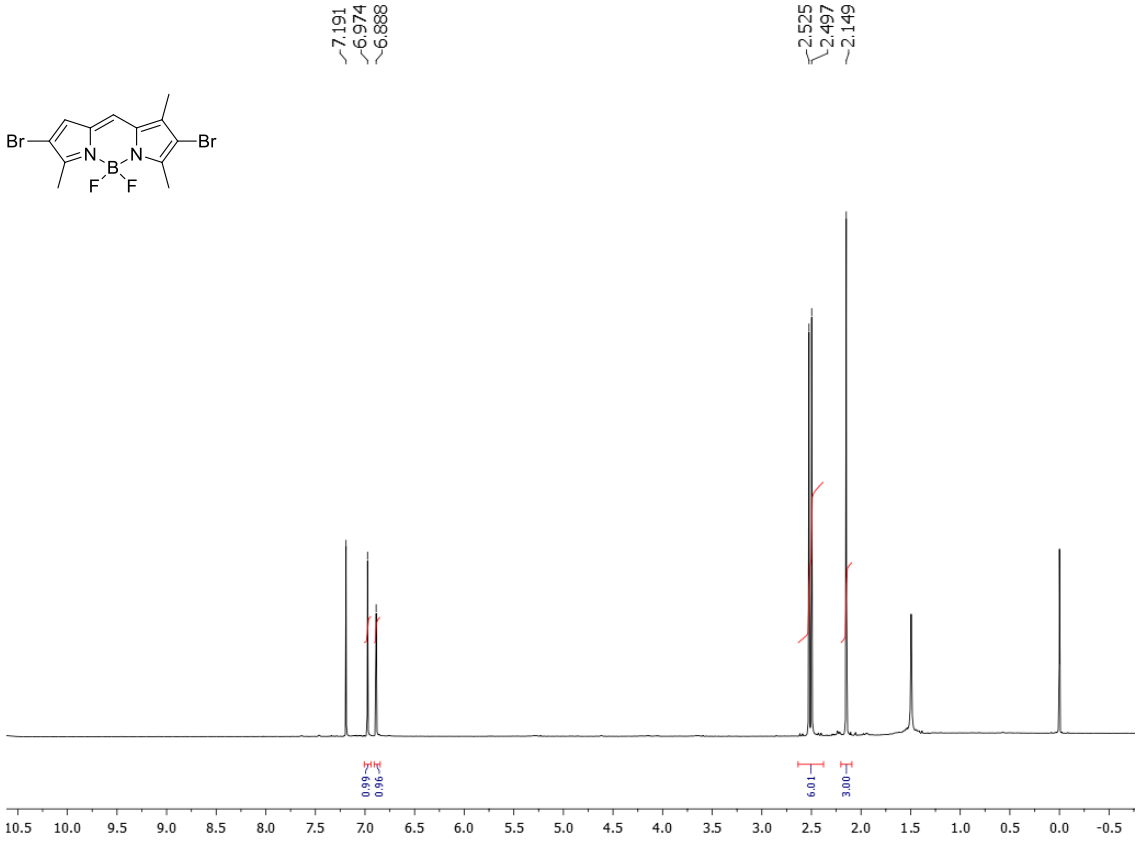


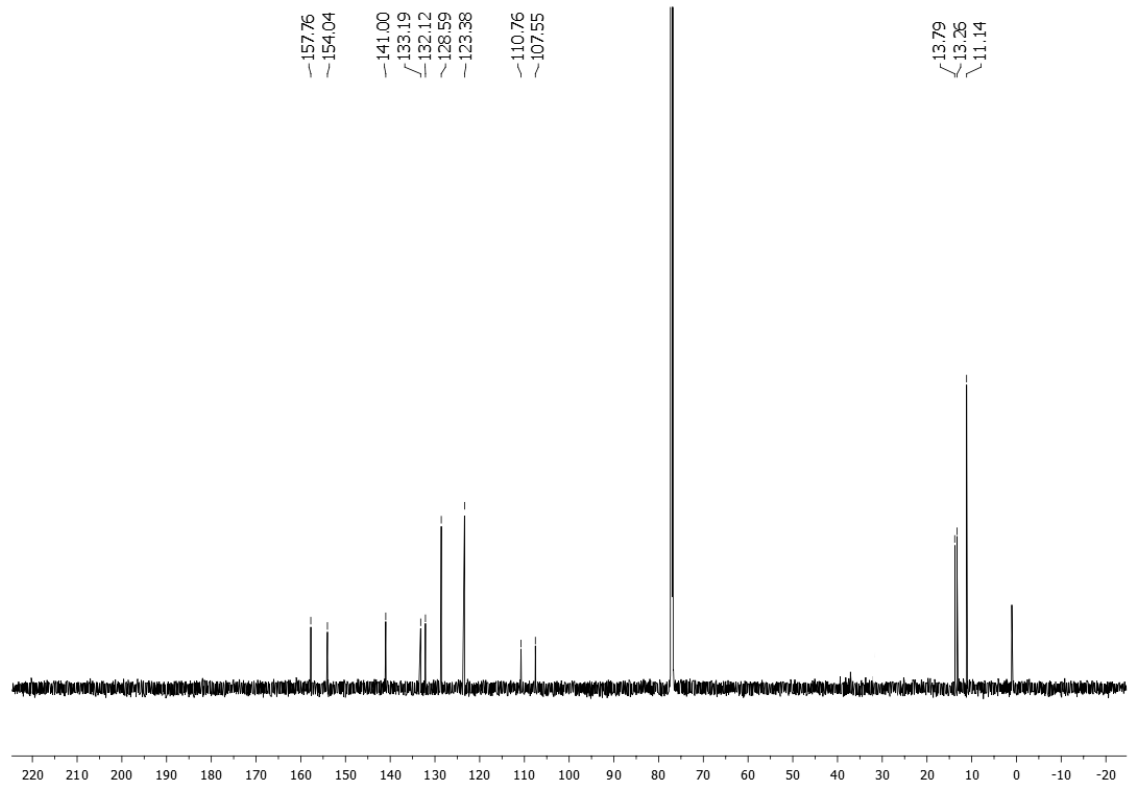
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **18**



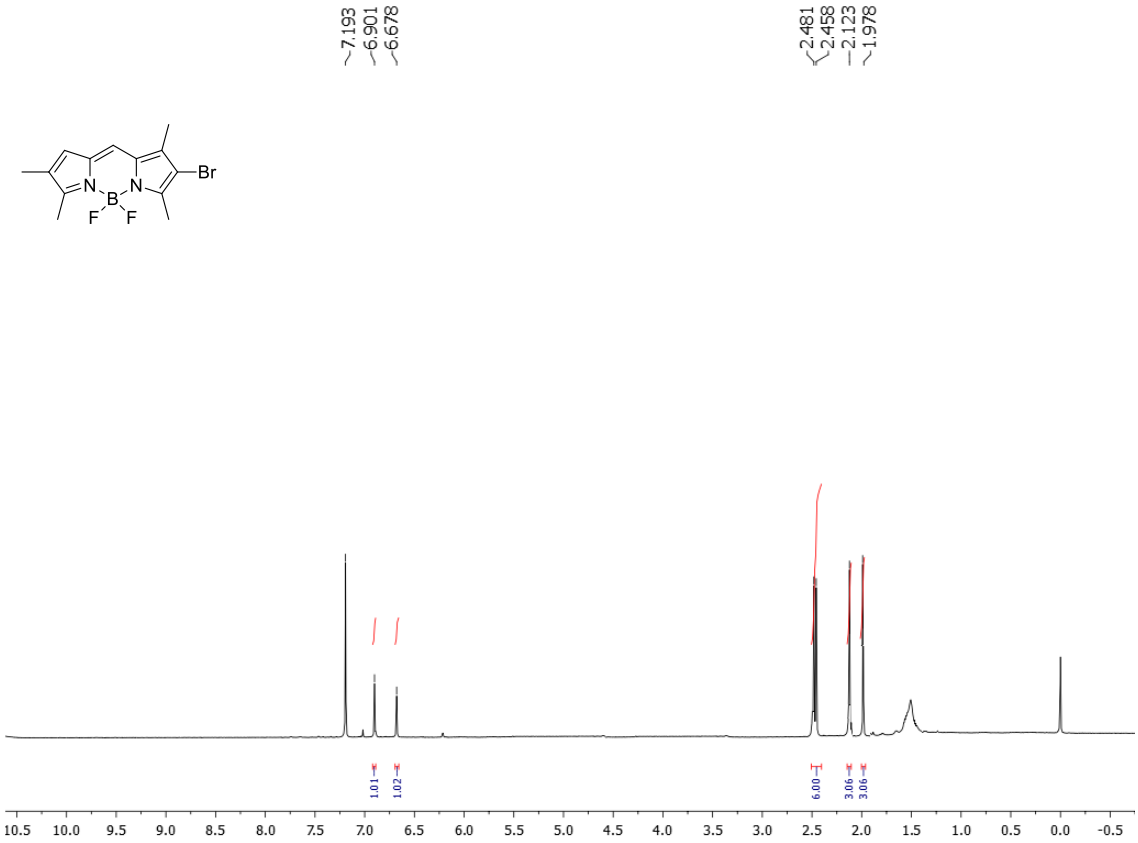


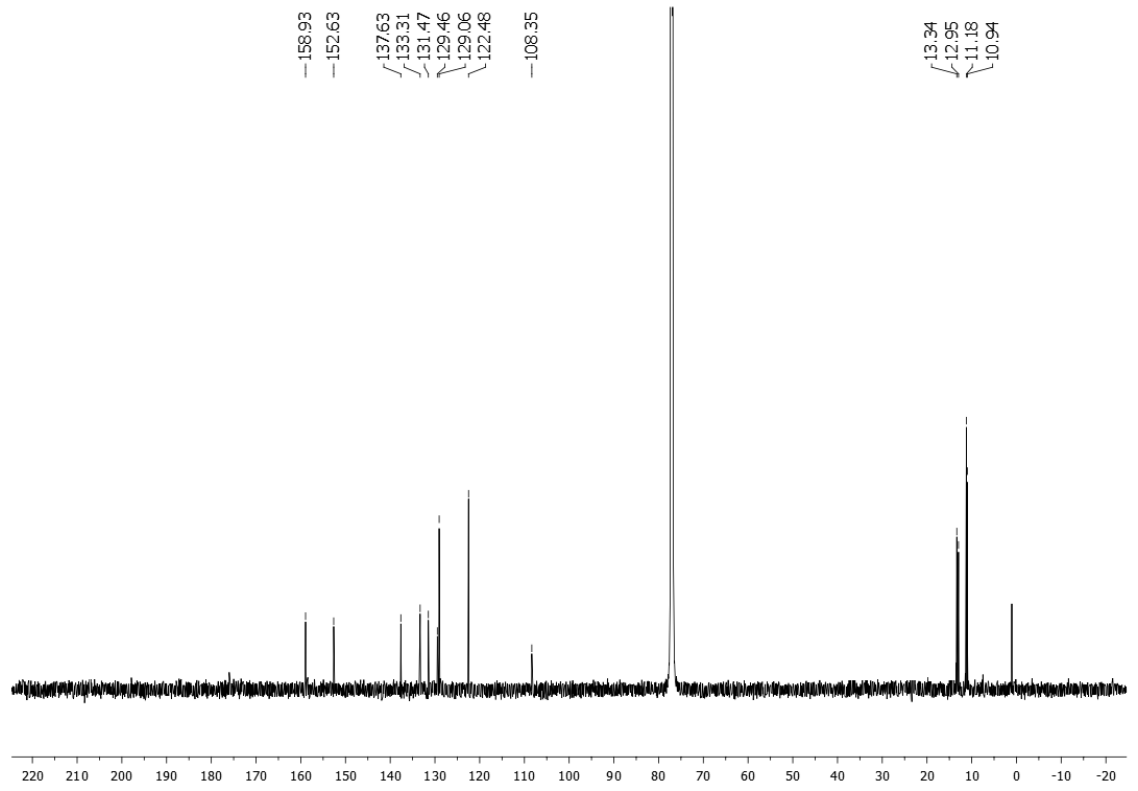
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **19**



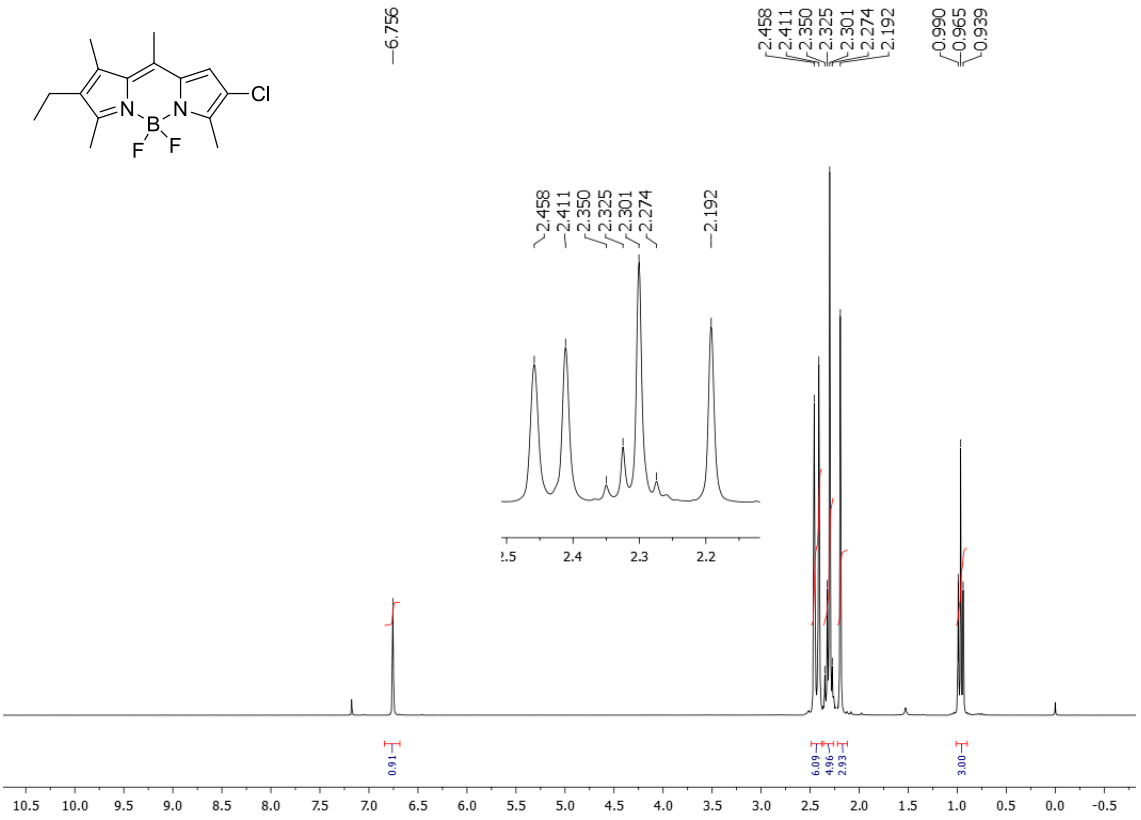


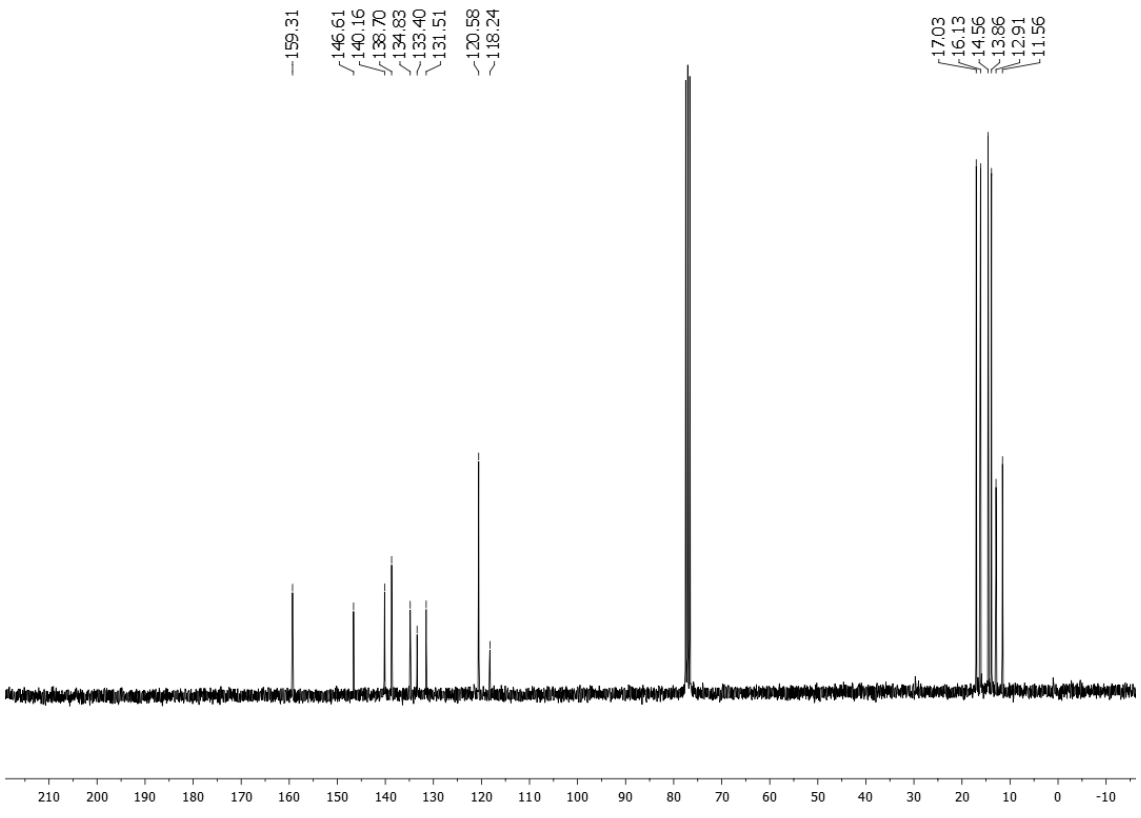
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **20**



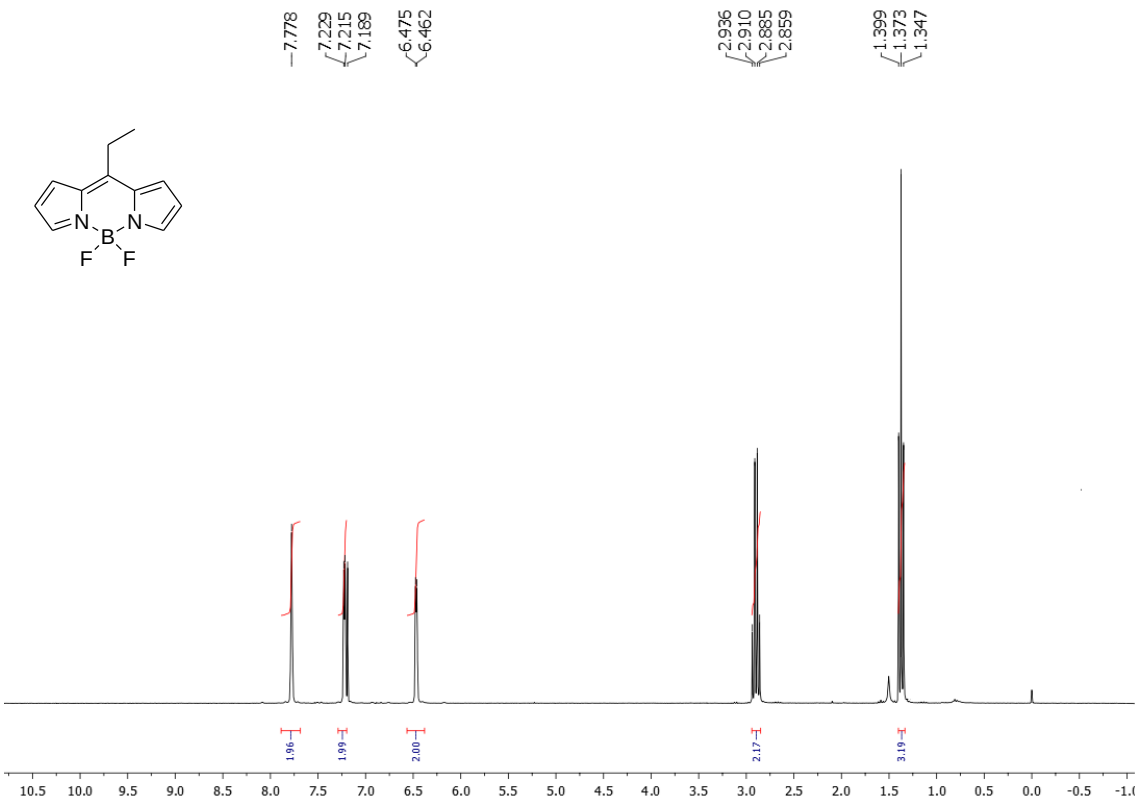


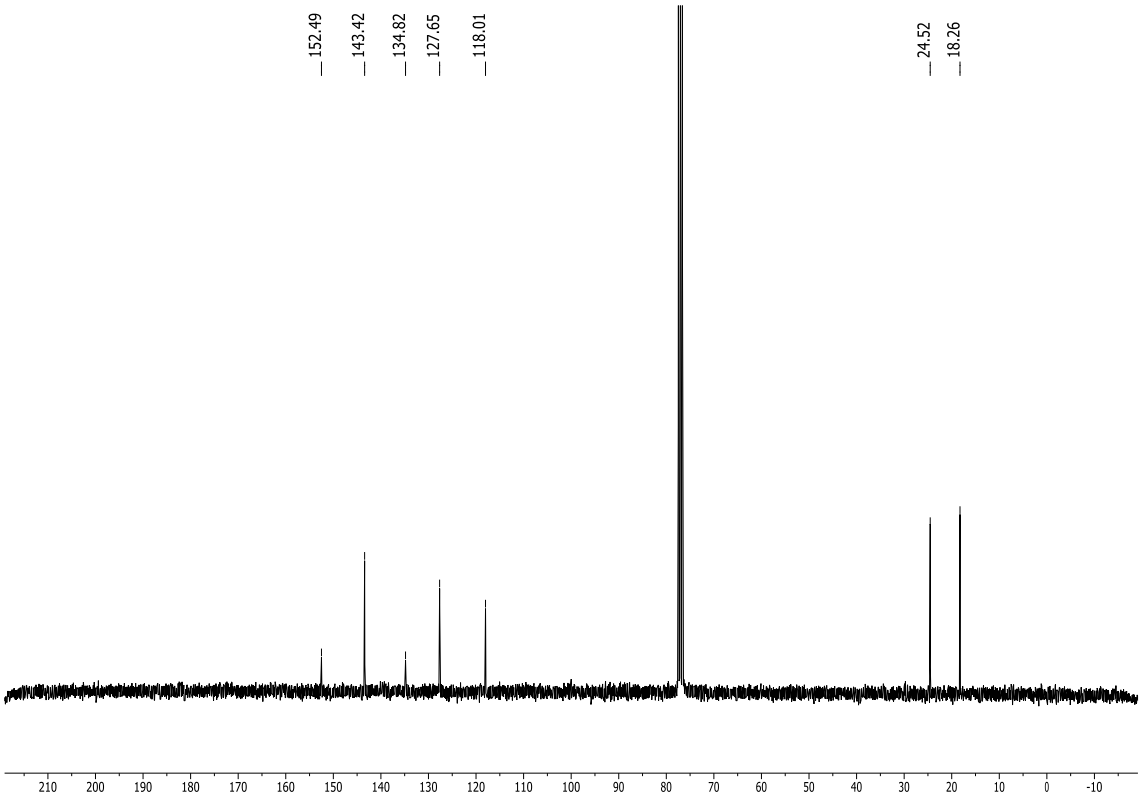
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of **21**



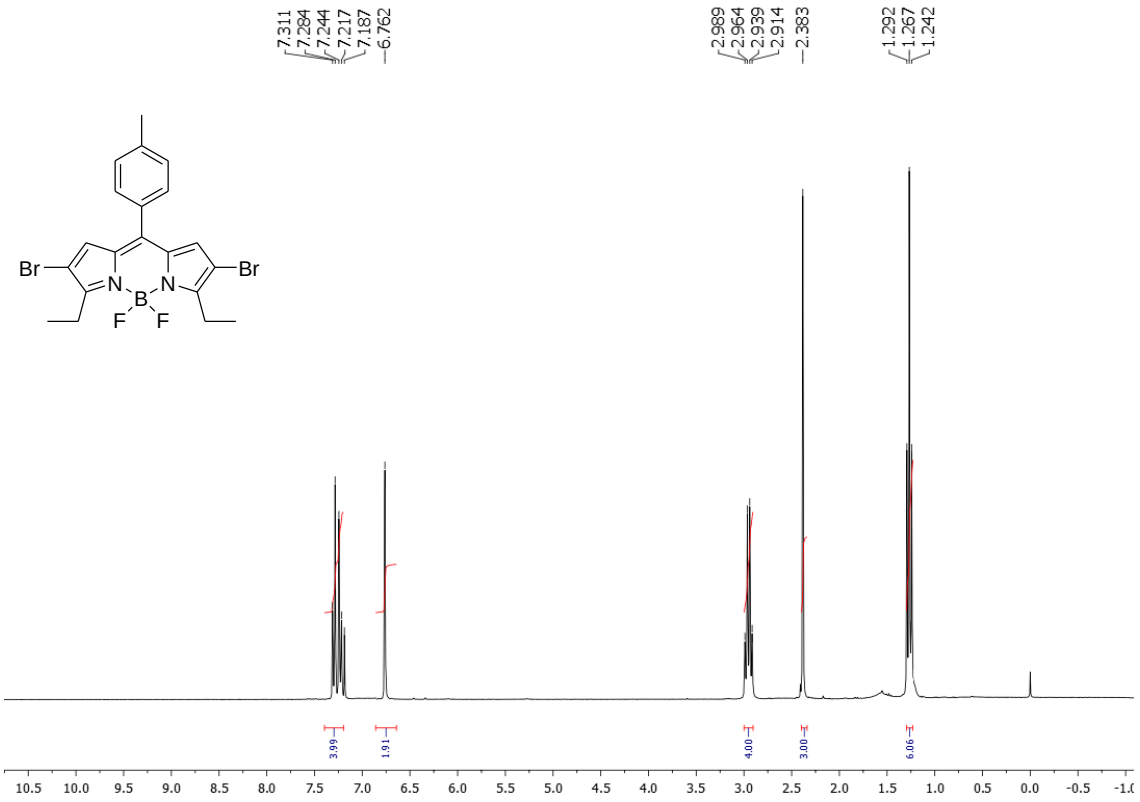


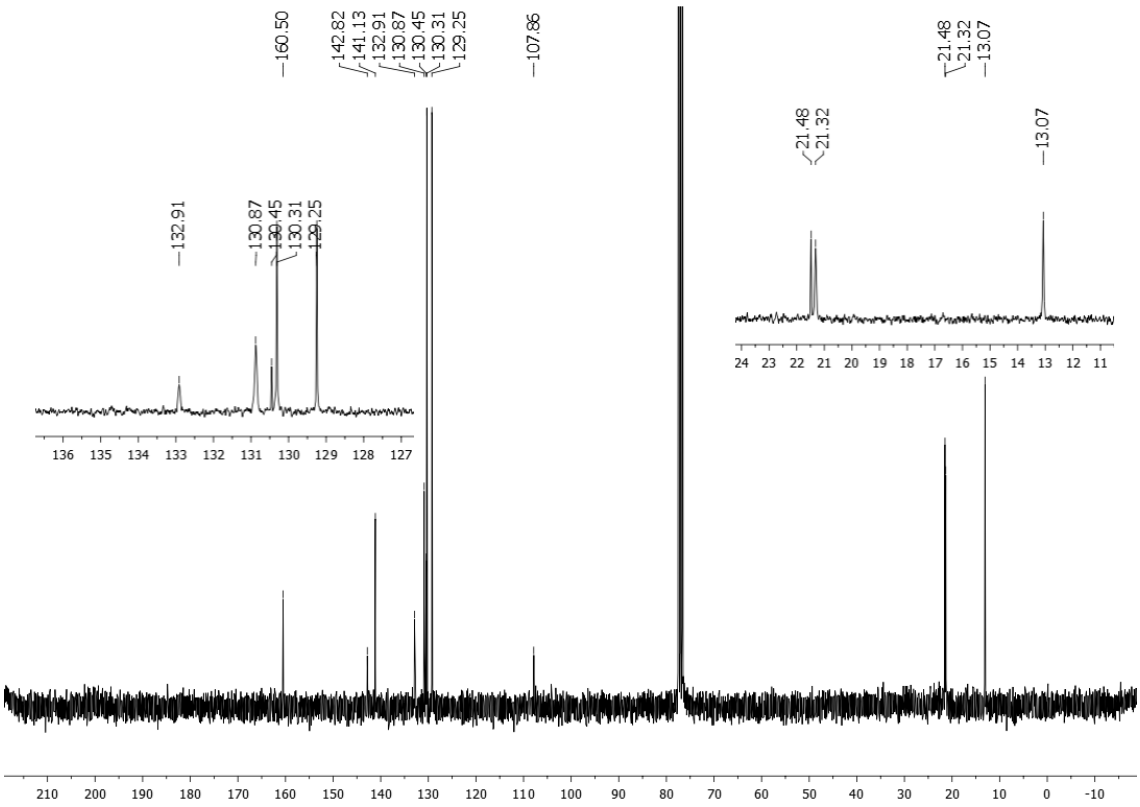
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of **25**



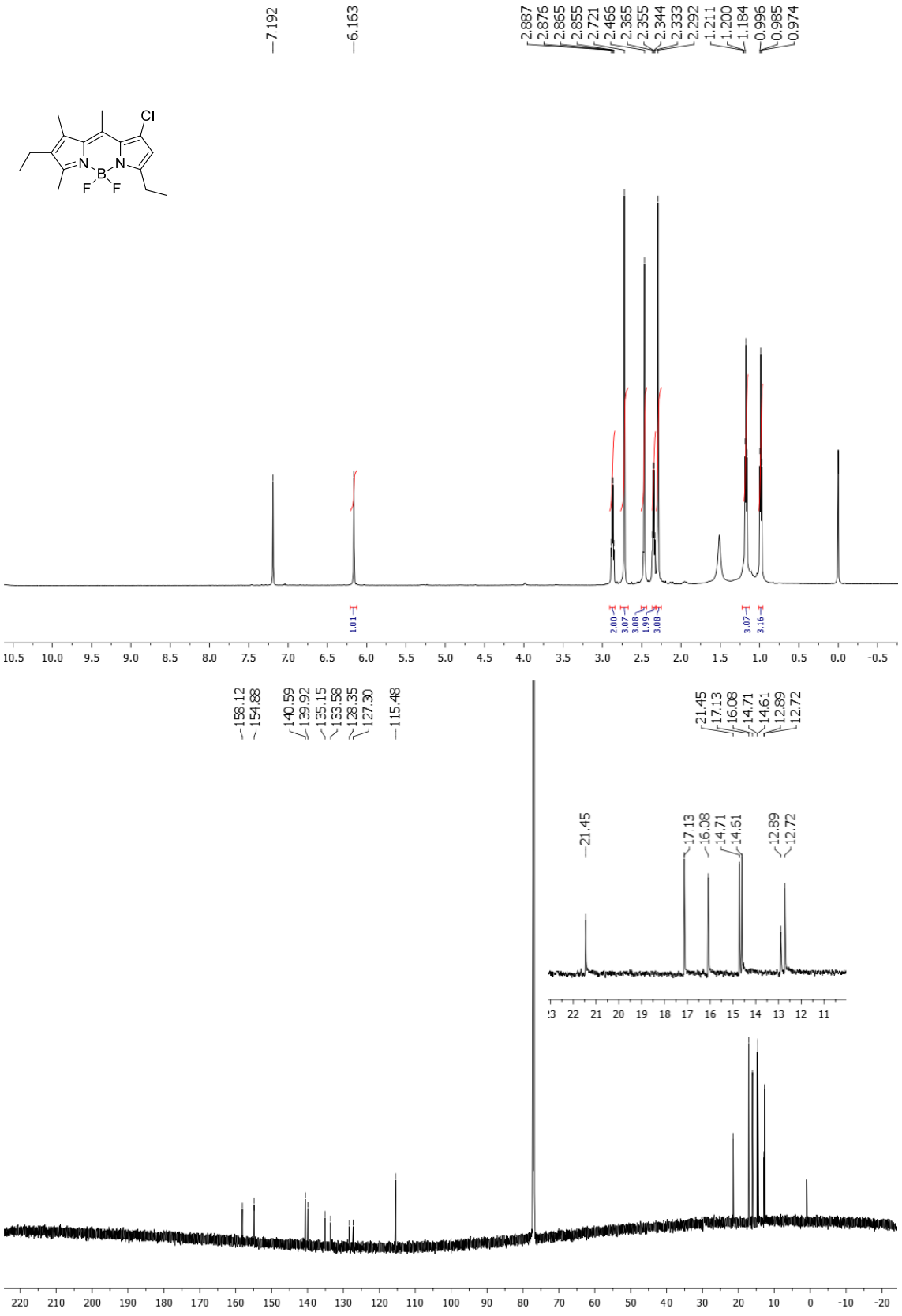


^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of **26**

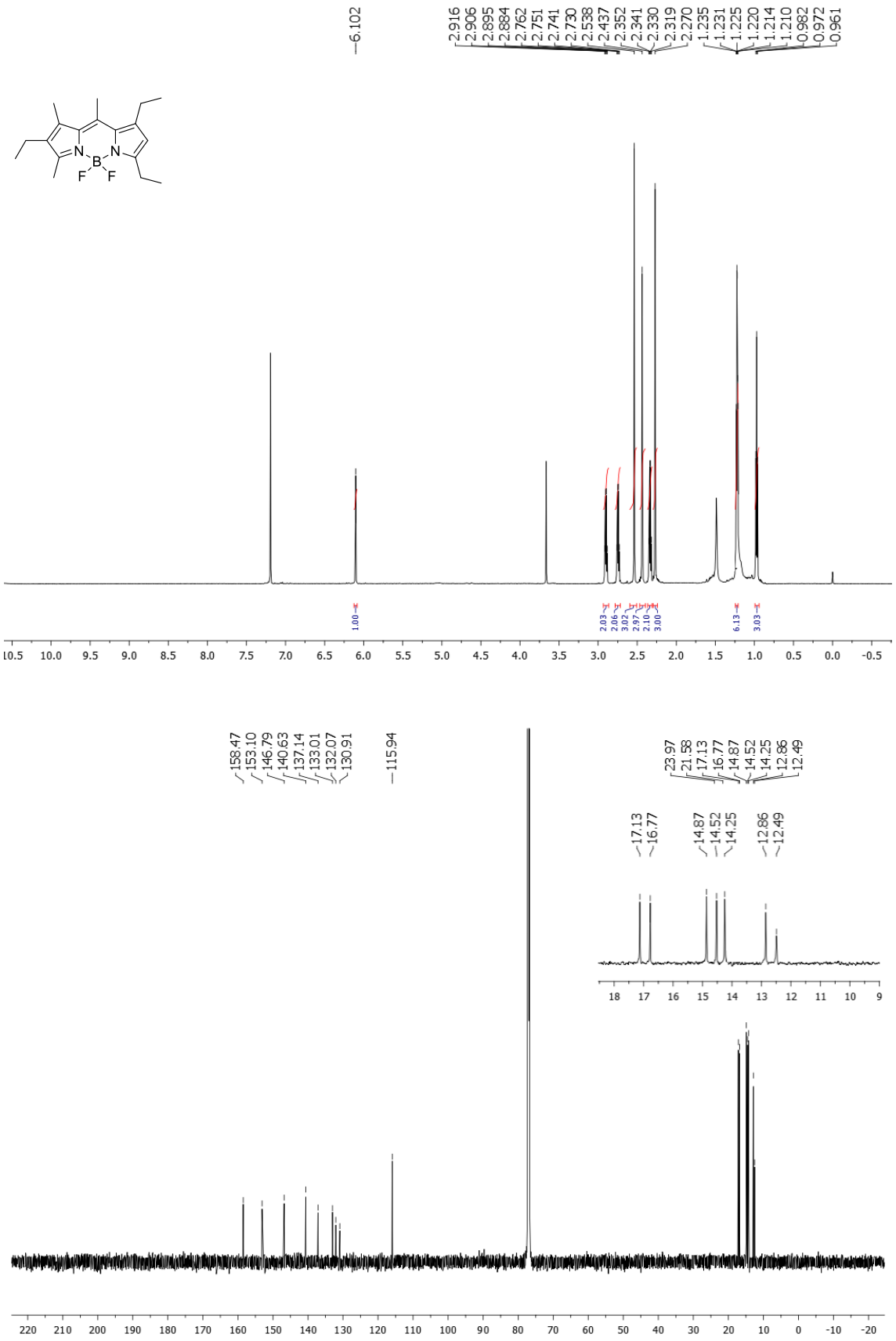




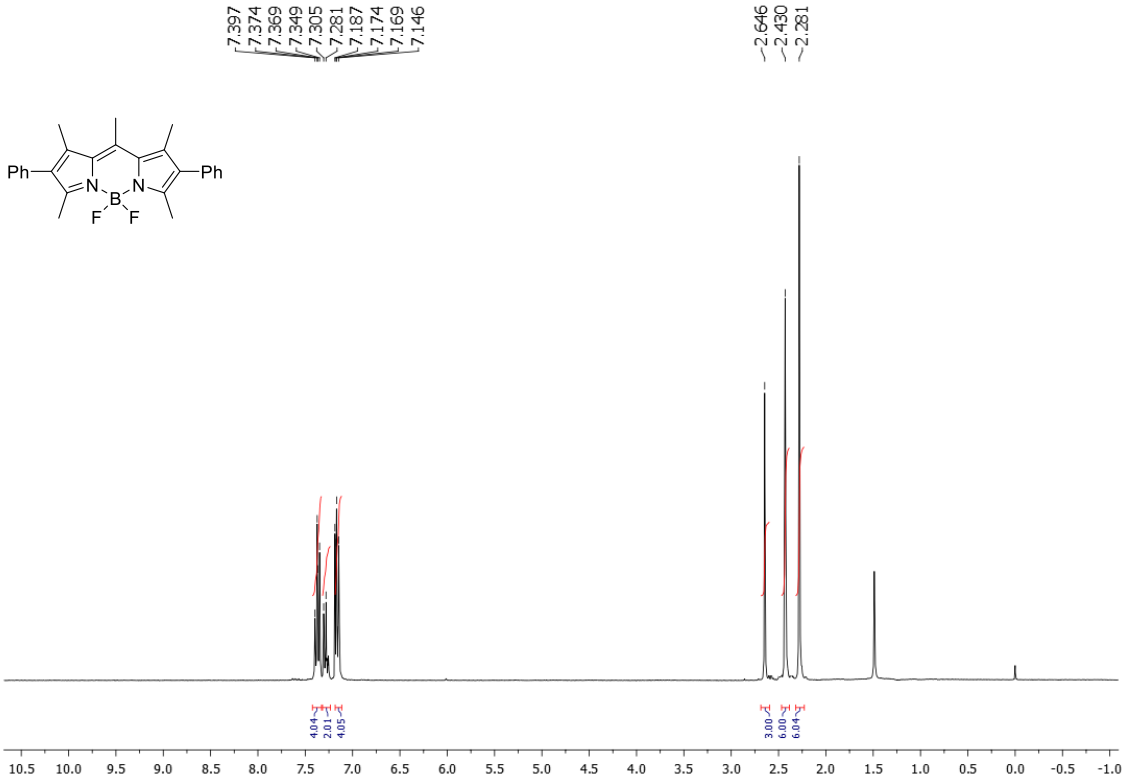
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **27**



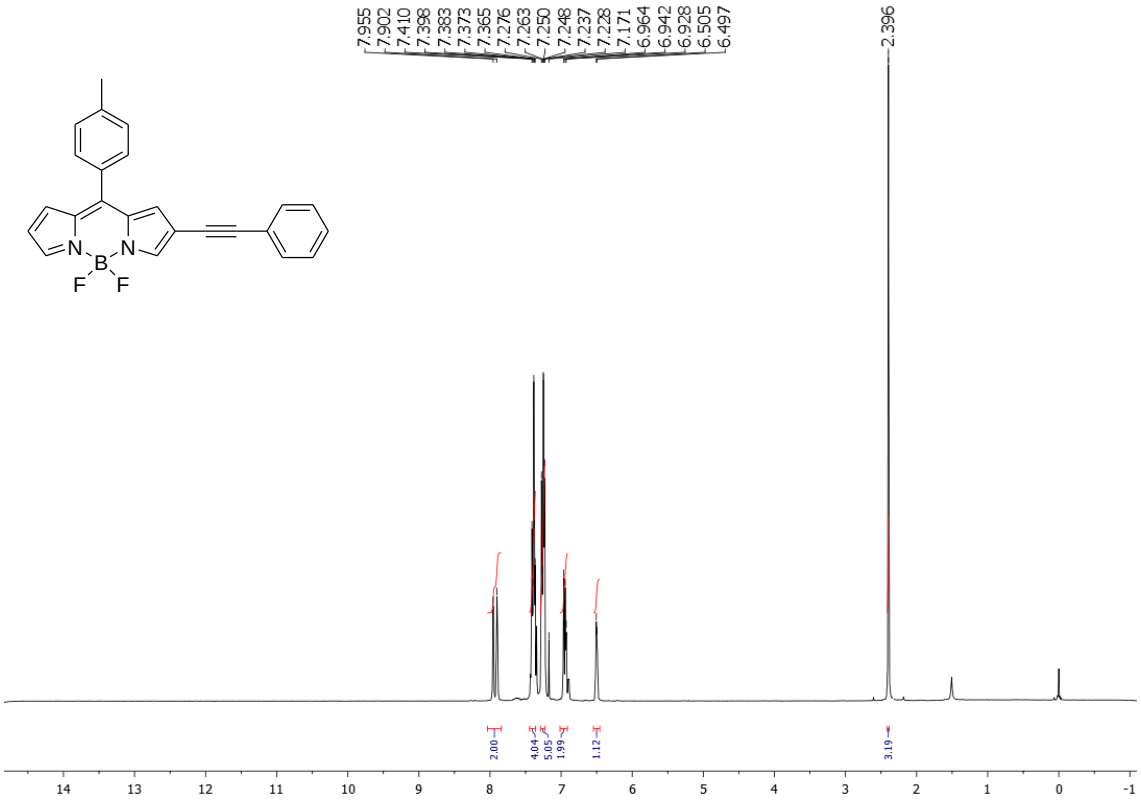
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **28**

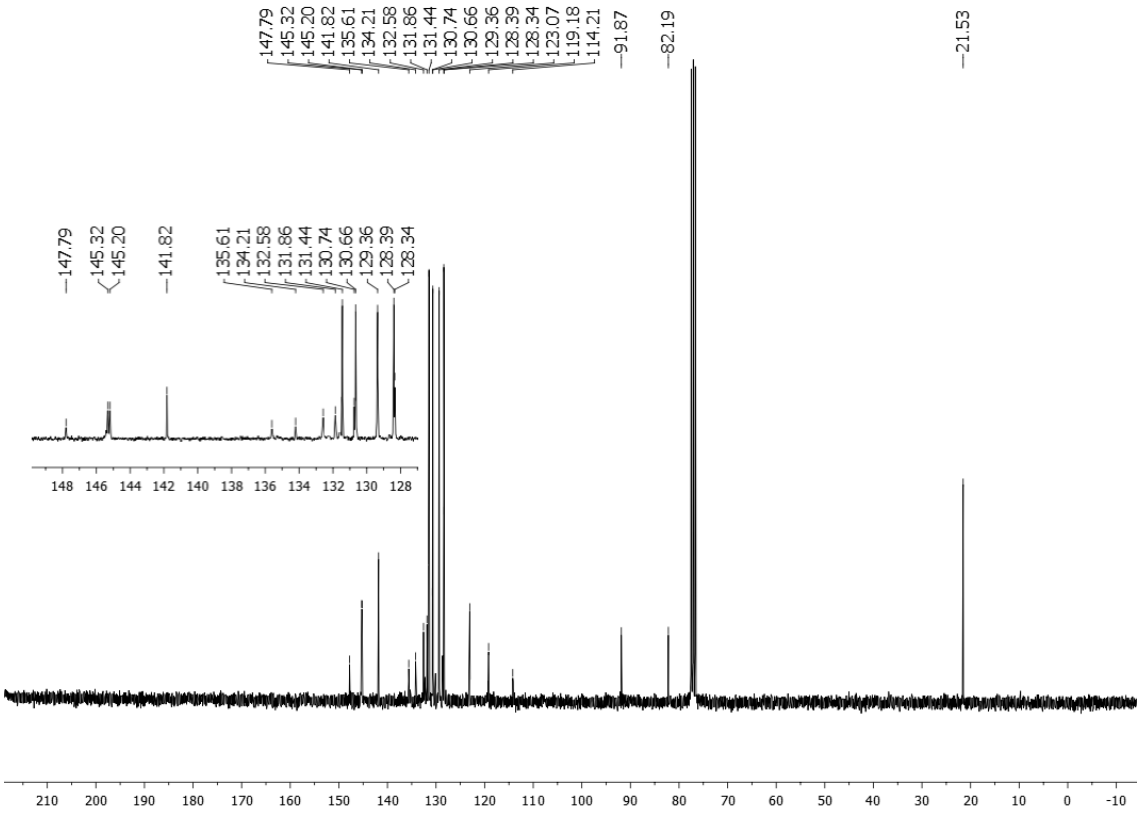


^{1}H NMR (300 MHz, $CDCl_3$) spectrum of known **29**[2]

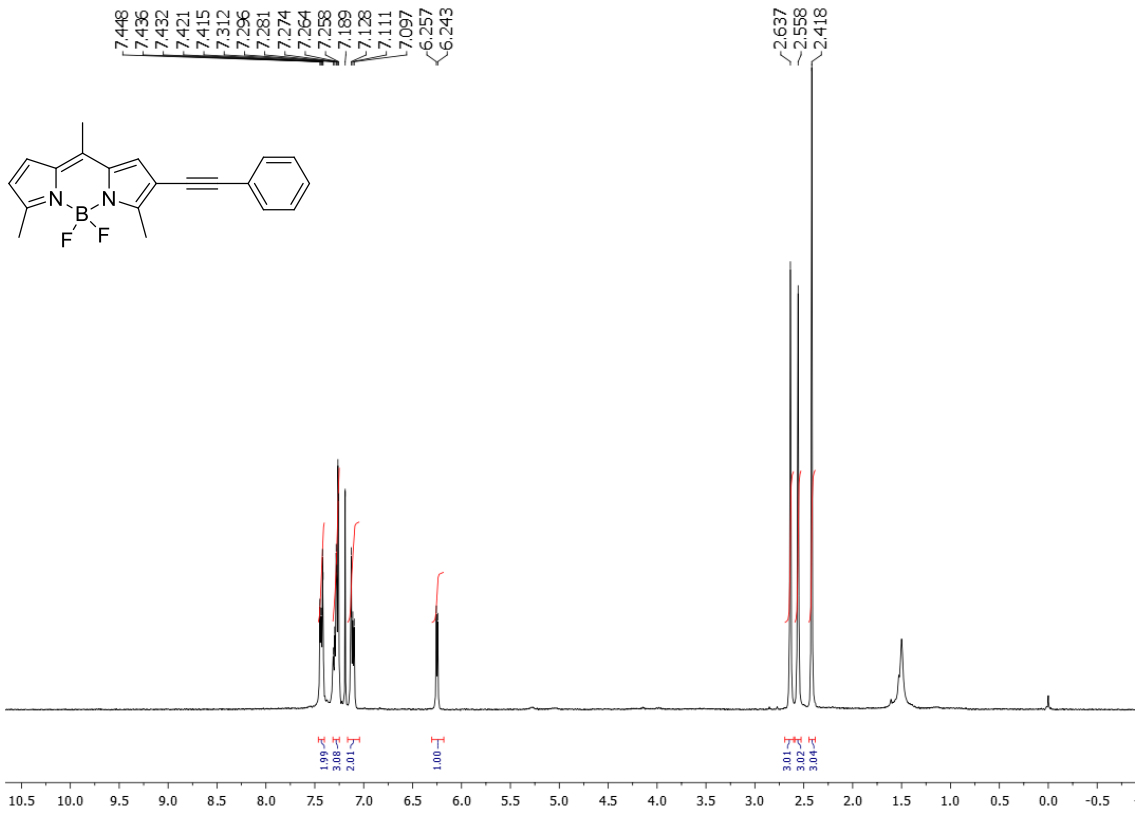


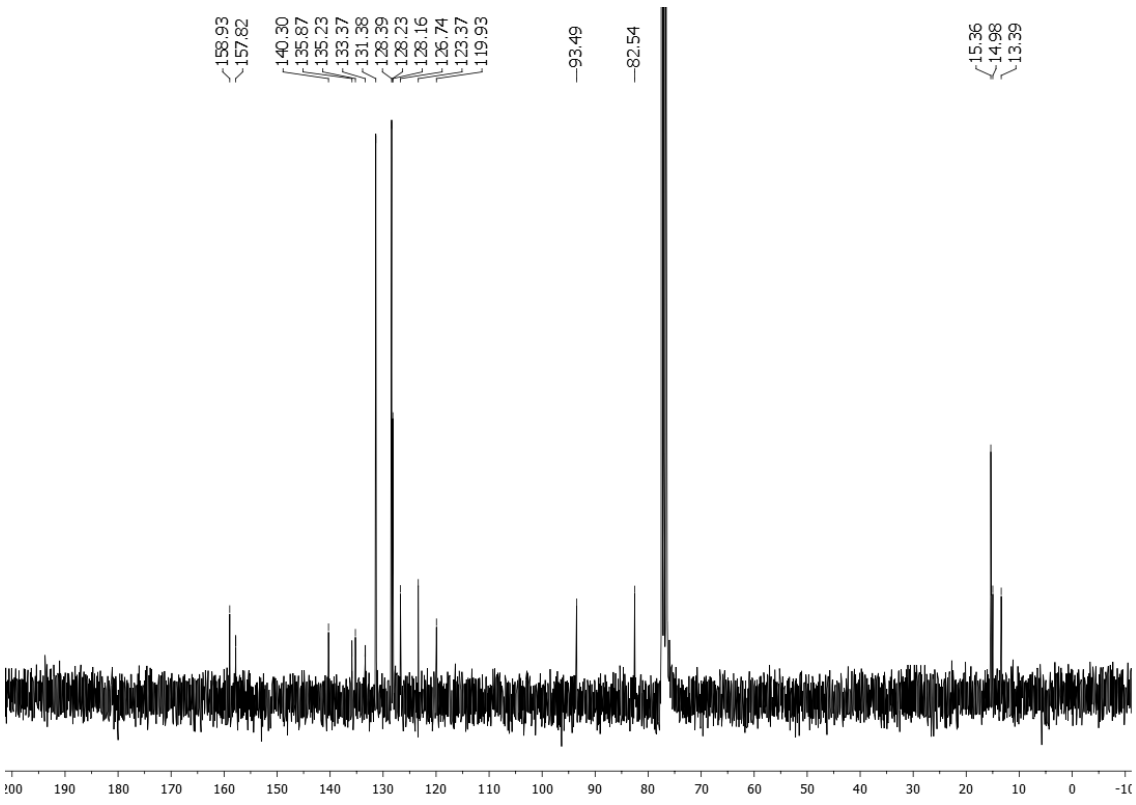
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of **30a**



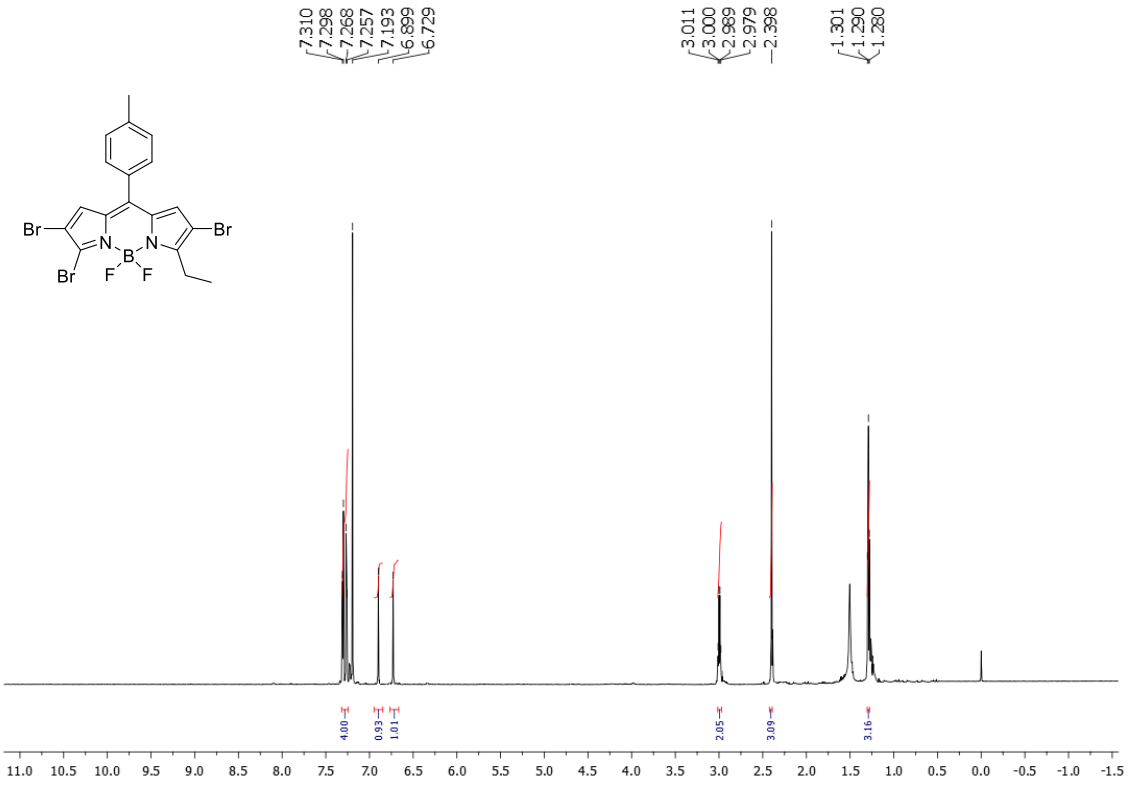


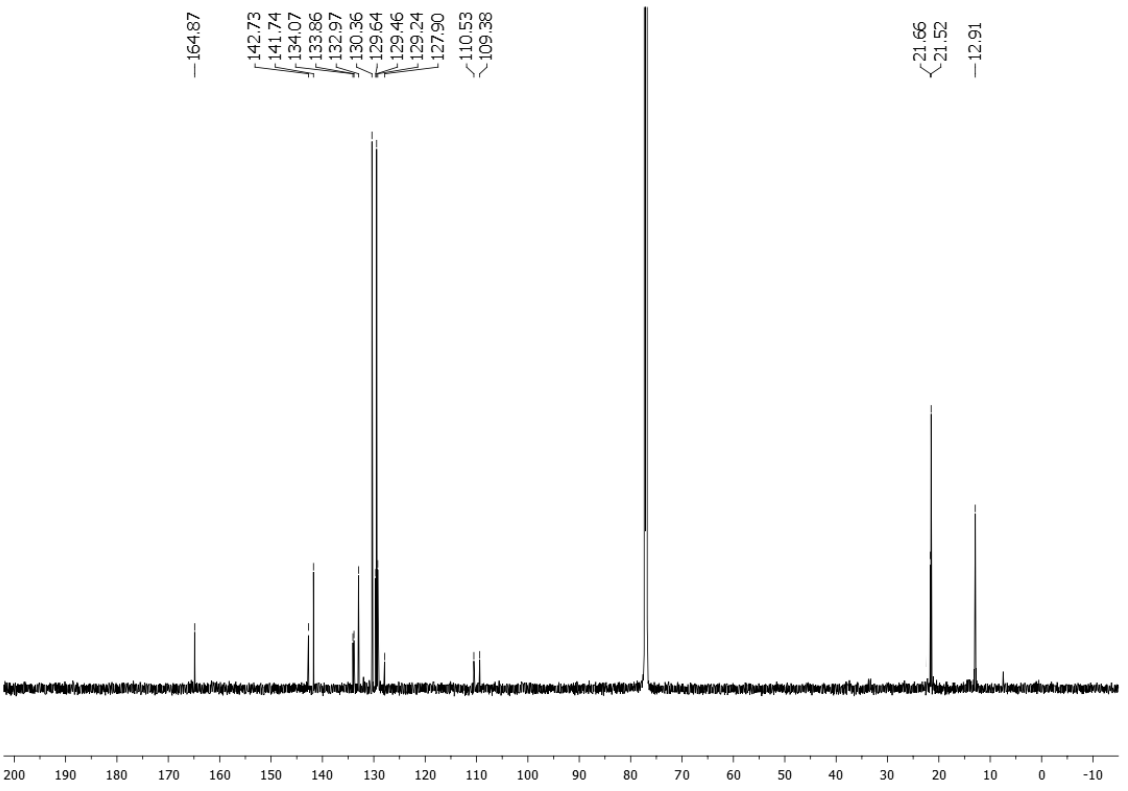
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of **30b**



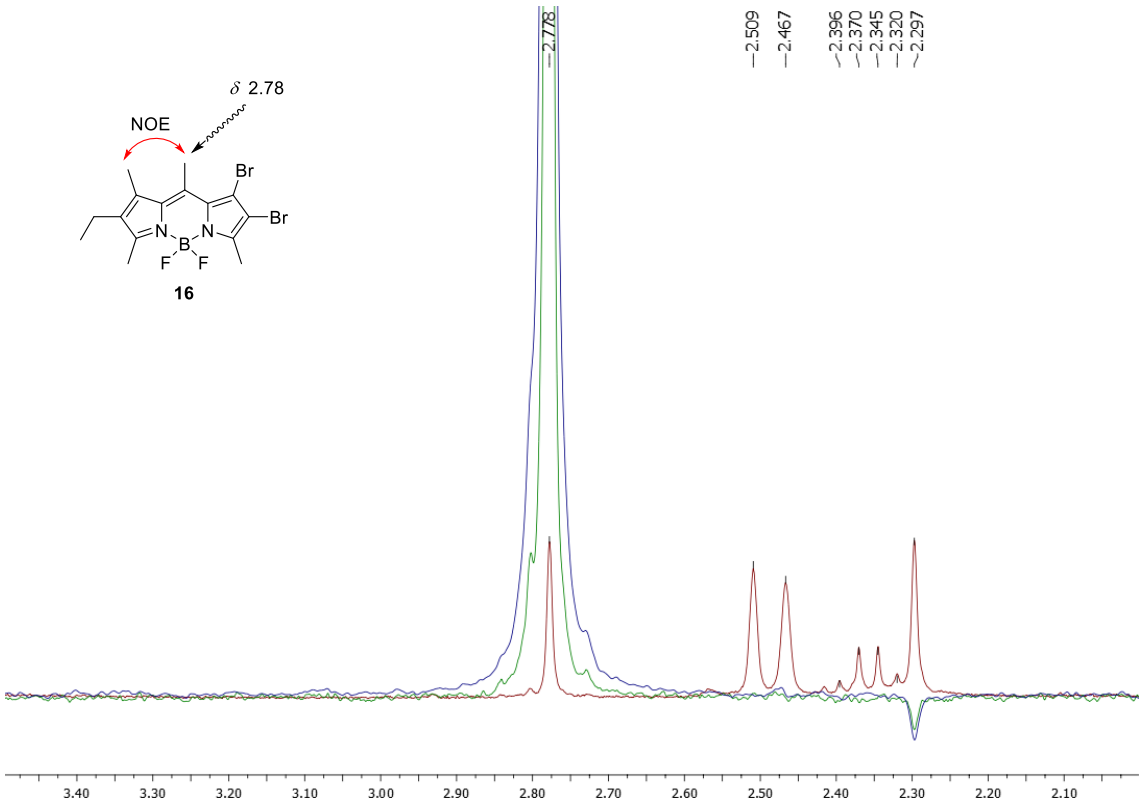


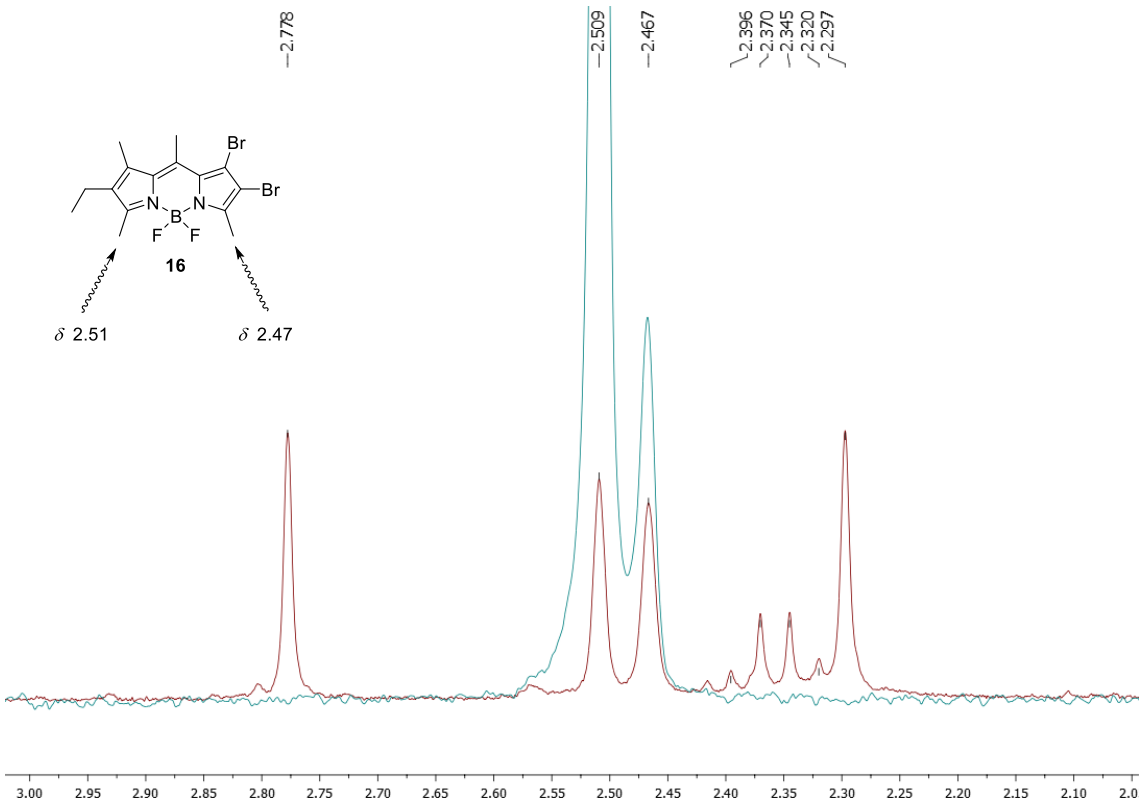
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) NMR spectra of **31**

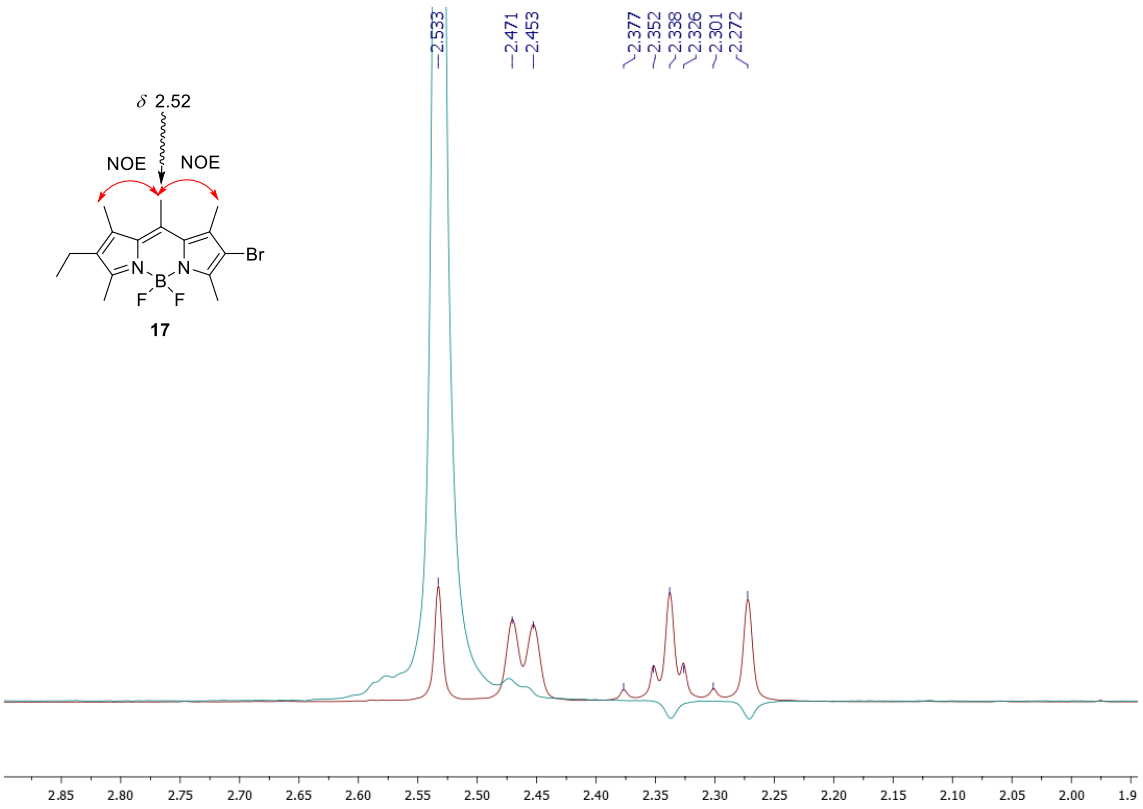


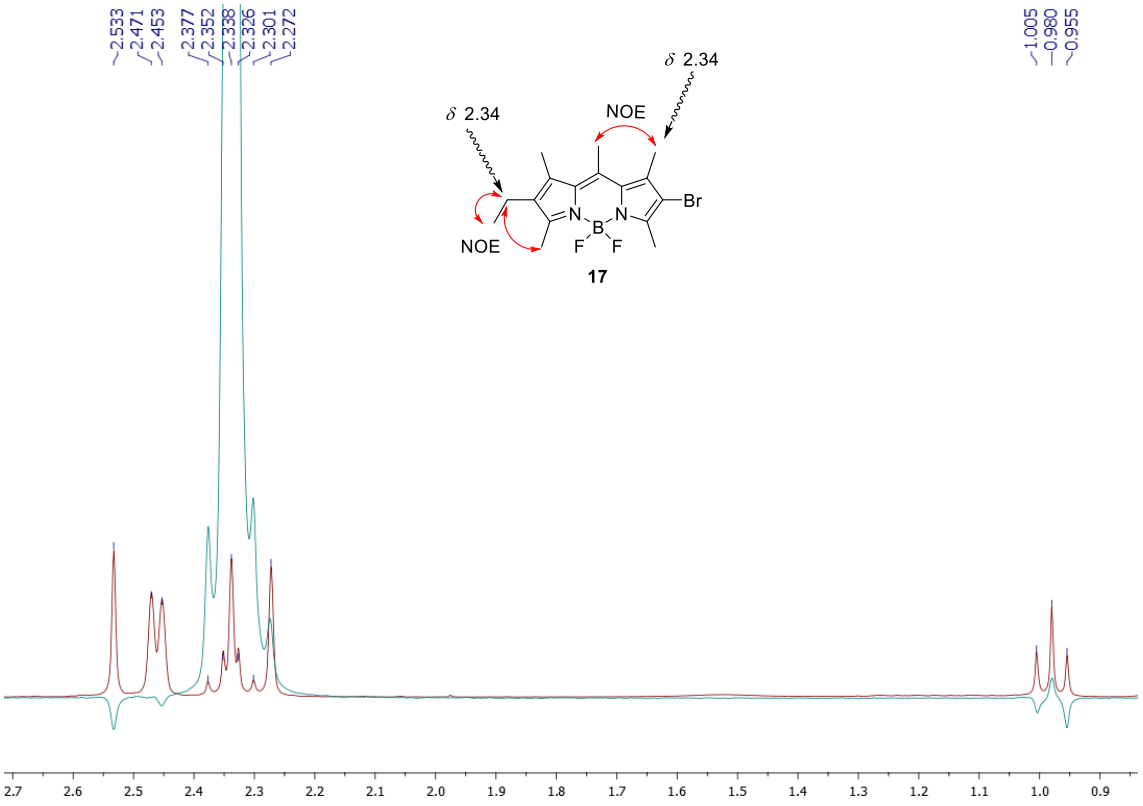


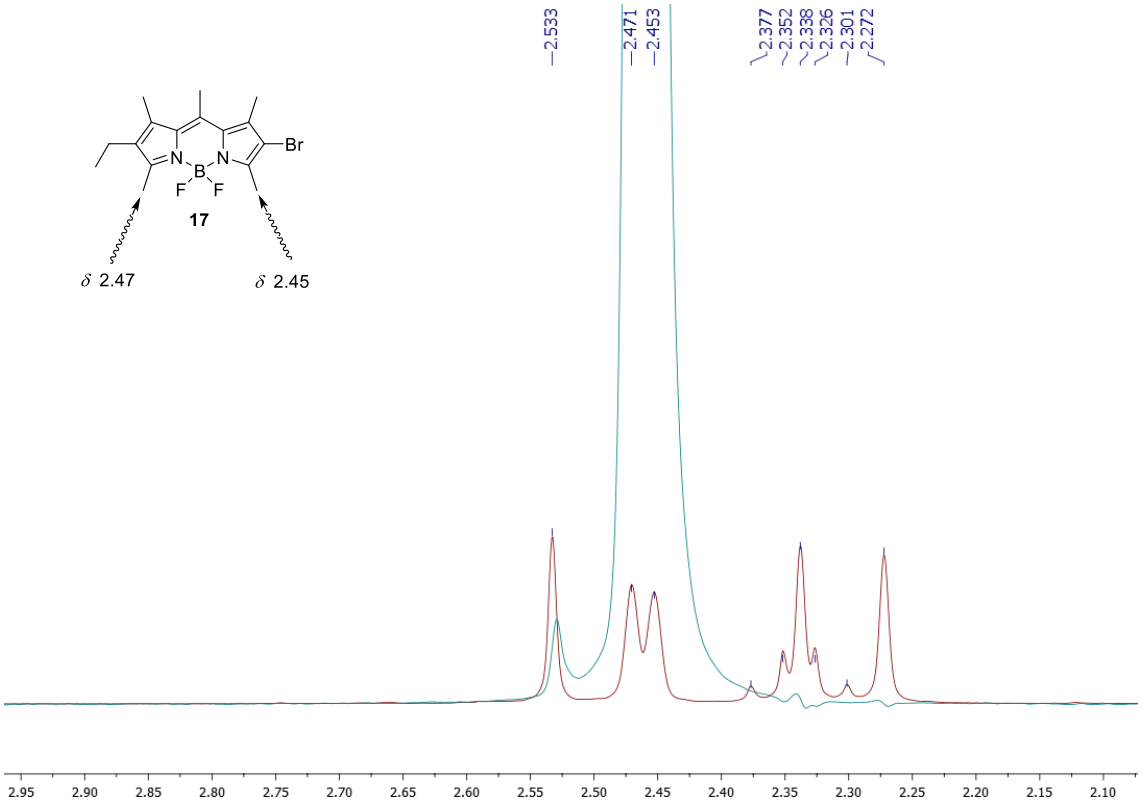
2. 1D NOESY Spectra (in green)

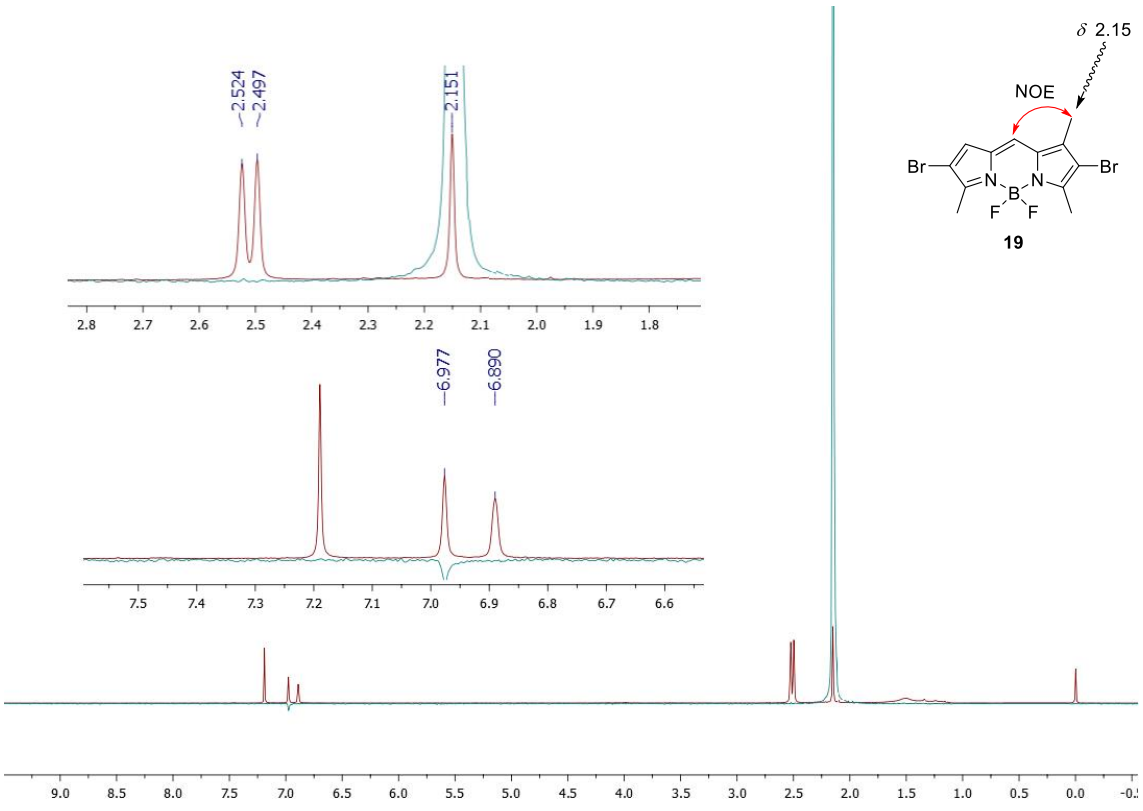


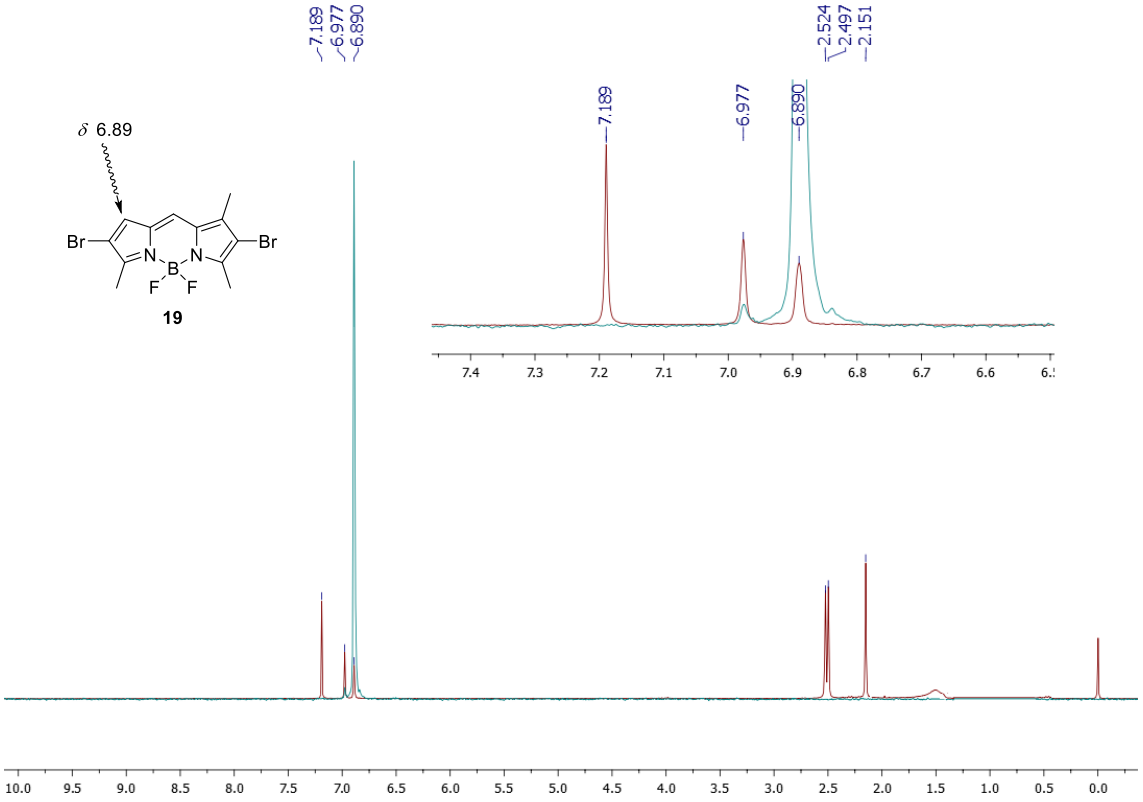


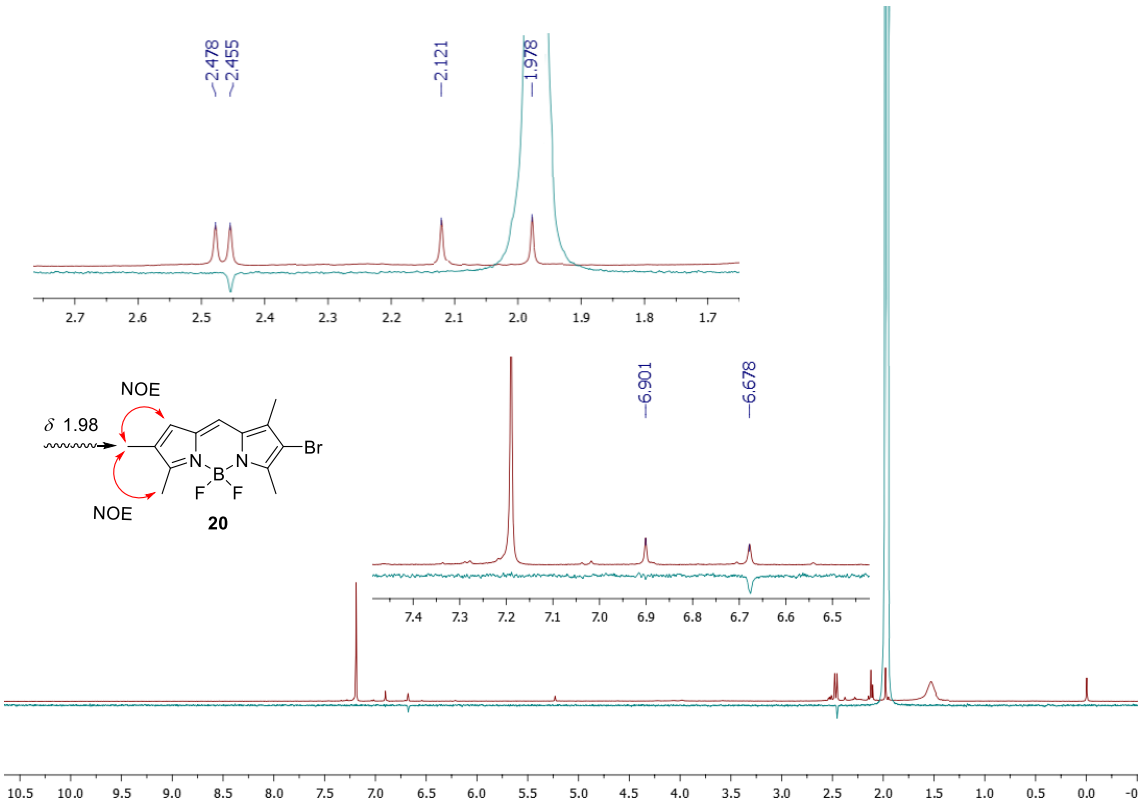

2.533
2.471
2.453
2.377
2.352
2.338
2.326
2.301
2.272
δ 2.52
NOE
NOE
Br
N
B
N
F
F
17
2.85 2.80 2.75 2.70 2.65 2.60 2.55 2.50 2.45 2.40 2.35 2.30 2.25 2.20 2.15 2.10 2.05 2.00 1.9

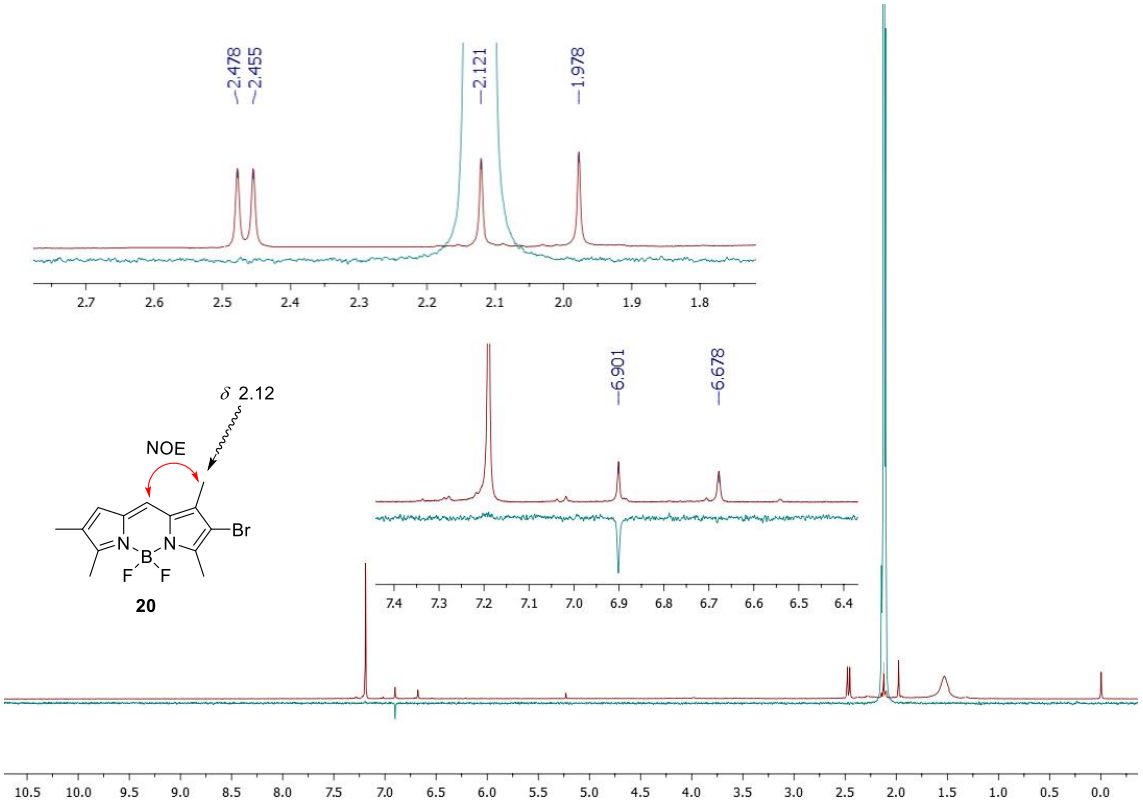

2.533
2.471
2.453
2.377
2.352
2.338
2.326
2.301
2.272
1.005
0.980
0.955
δ 2.34
δ 2.34
NOE
NOE
Br
N
B
N
F
F
17
2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9


2.533
2.471
2.453
2.377
2.352
2.338
2.326
2.301
2.272
Br
N
B
N
F
F
17
δ 2.47
δ 2.45
2.95 2.90 2.85 2.80 2.75 2.70 2.65 2.60 2.55 2.50 2.45 2.40 2.35 2.30 2.25 2.20 2.15 2.10


δ 2.15
NOE
2.524
2.497
2.151
6.977
6.890
Br
Br
N
B
N
F
F
19
2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

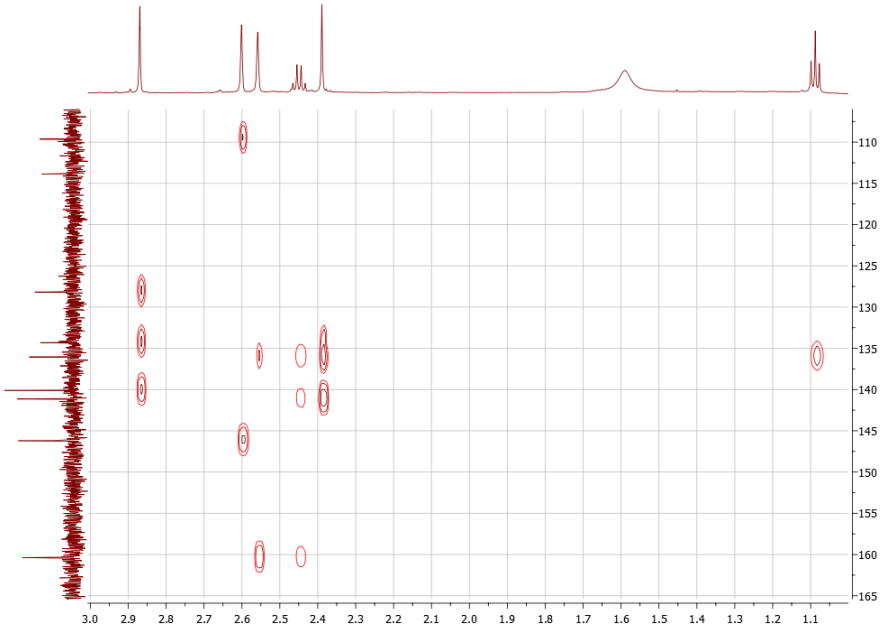

δ 6.89
Br
Br
N
B
N
F
F
19
7.189
6.977
6.890
2.524
2.497
2.151


2.478
2.455
2.121
1.978
NOE
δ 1.98
NOE
Br
N
B
N
F
F
20
6.901
6.678

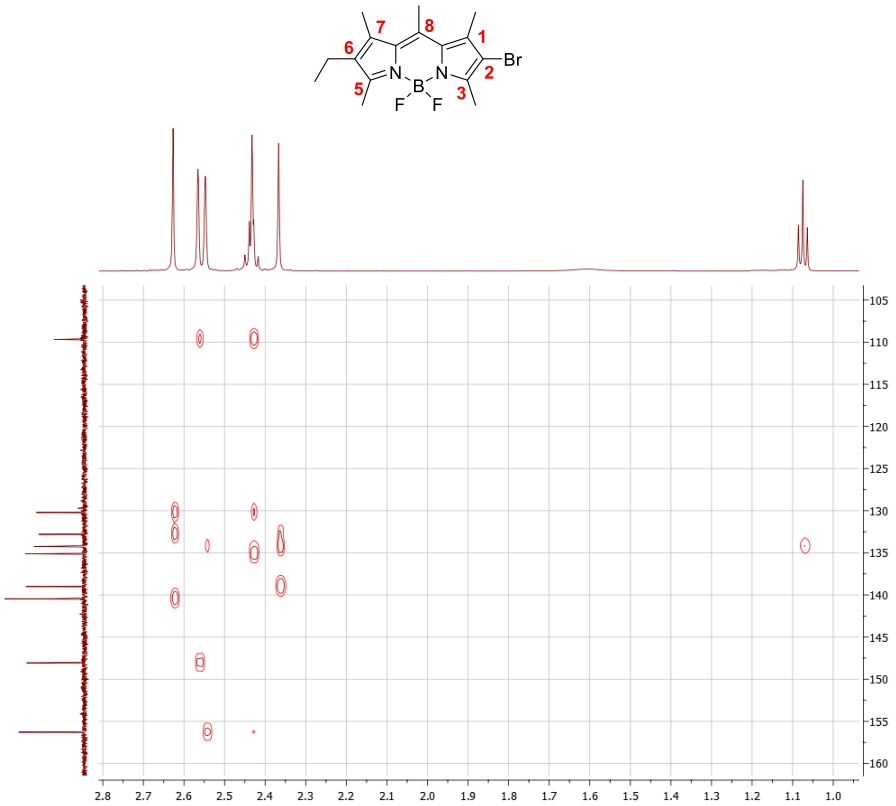

2.478
2.455
2.121
1.978
6.901
6.678
δ 2.12
NOE
Br
N
B
N
F
F
20

3. 2D HMBC Spectra

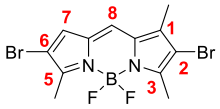
HMBC spectrum of **16**

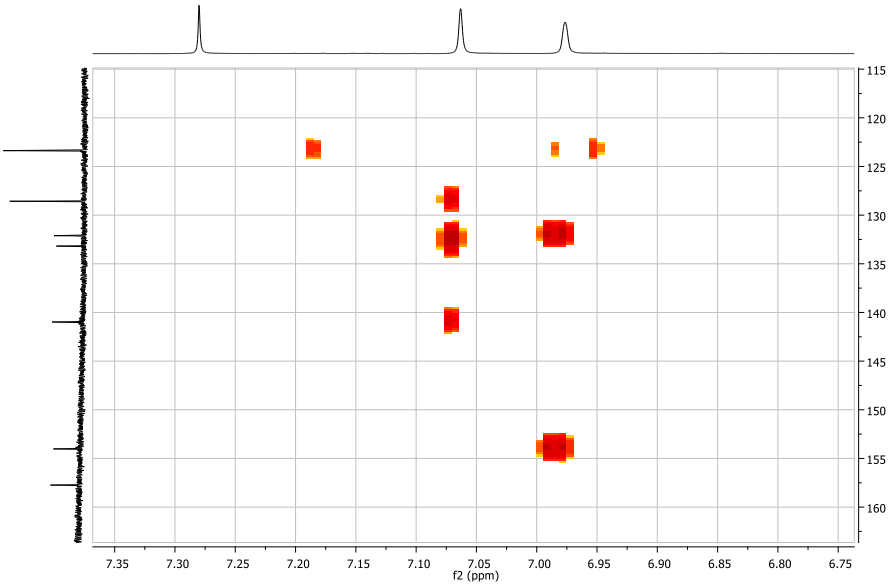


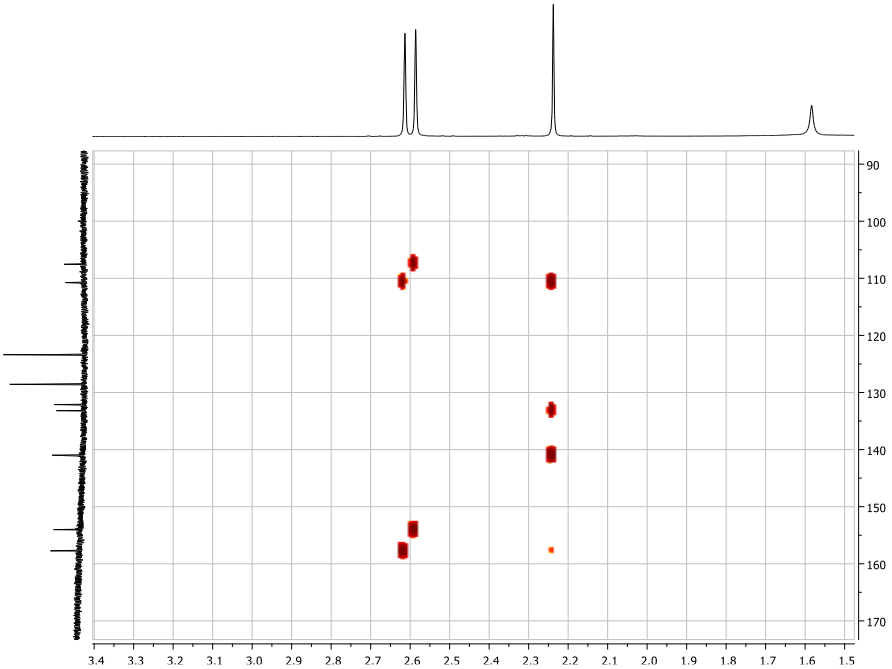
HMBC spectrum of **17**



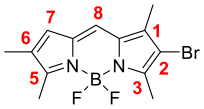
HMBC spectra of **19**

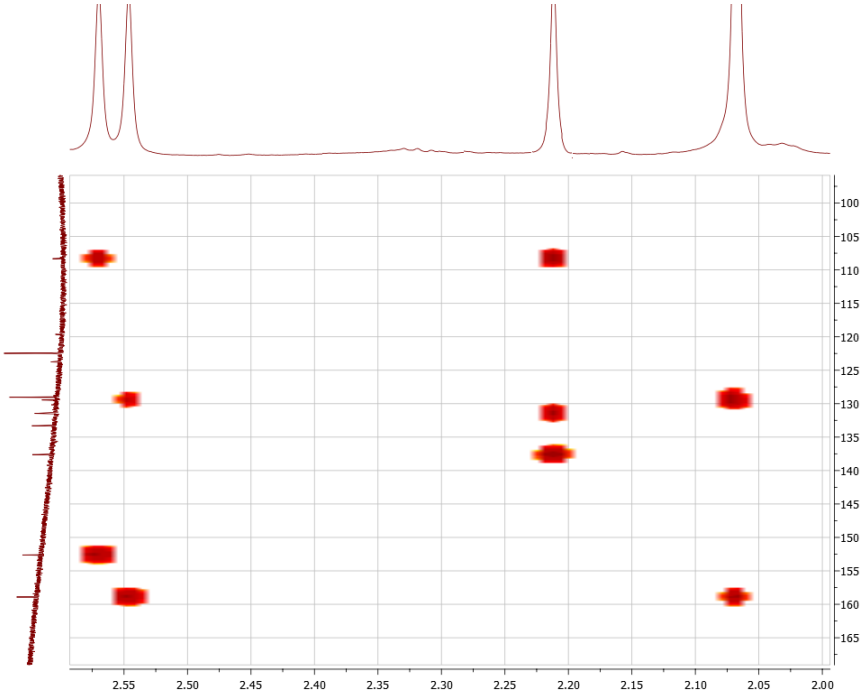


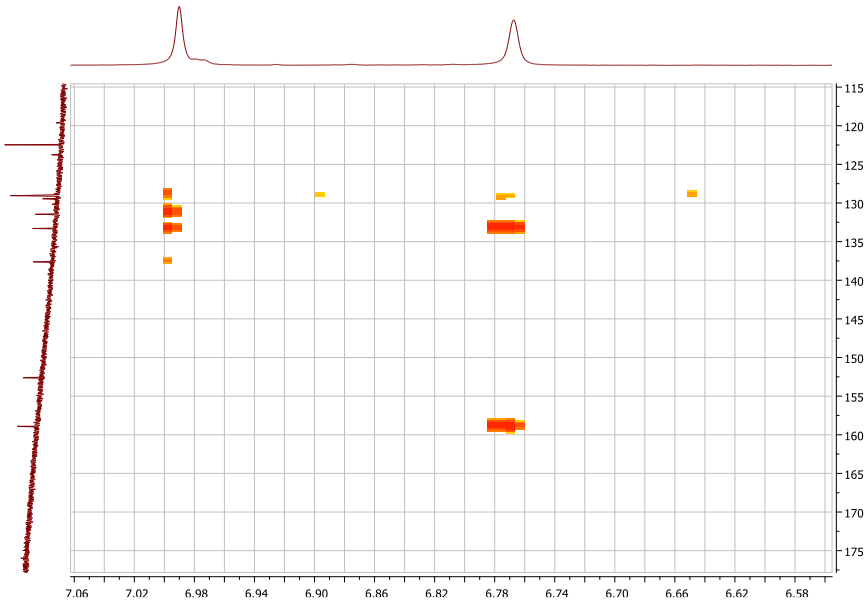




HMBC spectra of **20**







References

1. Leen, V.; Miscoria, D.; Yin, S.; Filarowski, A.; Ngongo, J. M.; Van der Auweraer, M.; Boens, N.; Dehaen, W. *J. Org. Chem.* **2011**, *76*, 8168-8176.

2. Boyer, J. H.; Haag, A. M.; Sathyamoorthi, G.; Soong, M. L.; Thangaraj, K.; Pavlopoulos, T. G. *Heteroatom Chem.* **1993**, *4*, 39-49.